THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ANNUAL GENERAL MEETING

THE eighty-sixth Annual General Meeting of the Society was held at 4.30 p.m. on Wednesday, March 2nd, 1960, at the Queen's Hotel, Stephenson Place, Birmingham, 2. The Chair was occupied by the President, Mr. R. C. Chirnside, F.R.I.C. The Financial Statement for the year ending October 31st, 1959, was presented by the Honorary Treasurer and approved, and the Auditors for 1960 were appointed. The Report of the Council for the year ending March, 1960 (see pp. 307–317), was presented by the Honorary Secretary and adopted.

The Scrutineers, Messrs. G. W. Cherry and C. A. Johnson, reported that the following had been elected officers for the coming year—

President—R. C. Chirnside, F.R.I.C

Past Presidents serving on the Council—J. H. Hamence, D. W. Kent-Jones, J. R. Nicholls and K. A. Williams.

Vice-Presidents—D. C. Garratt, Magnus A. Pyke and J. G. Sherratt.

Honorary Treasurer—A. J. Amos.

Honorary Secretary—R. E. Stuckey.

Honorary Assistant Secretaries—L. Brealey (Programmes Secretary) and S. A. Price.

Other Members of Council—The Scrutineers further reported that 149 valid ballot papers had been received. As the number of candidates for election as Ordinary Members of Council had been equal to the number of places to be filled, there had been no ballot for their election.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—D. M. W. Anderson, B. Bagshawe, E. Bishop, E. Q. Laws, W. M. Lewis and J. T. Yardley.

N. L. Allport, H. E. Brookes, C. H. R. Gentry, R. F. Milton, F. C. J. Poulton and C. Whalley, having been elected members of the Council in 1959, will, by the Society's Articles of Association, remain members of the Council for 1960.

J. R. Edisbury (Chairman of the North of England Section), A. N. Harrow (Chairman of the Scottish Section), G. V. James (Chairman of the Western Section), S. H. Jenkins (Chairman of the Midlands Section), F. Holmes (Chairman of the Microchemistry Group), G. W. C. Milner (Chairman of the Physical Methods Group) and J. I. M. Jones (Chairman of the Biological Methods Group) will be *ex-officio* members of the Council for 1960.

After the business outlined above had been completed, the meeting was opened to visitors, and Professor A. C. Frazer, M.D., D.Sc., Ph.D., F.R.C.P., delivered the Bernard Dyer Memorial Lecture (see pp. 332–340). At the close of the meeting the President presented Professor Frazer with the Bernard Dyer Memorial Medal.

JOINT SYMPOSIUM

A JOINT Symposium of the Society with the Fertiliser Society was held on Thursday and Friday, April 21st and 22nd, 1960, at Church House, Westminster, London, S.W.1. The subject of the Symposium was "Fertiliser Analysis."

The Chair at the first session, on the afternoon of April 21st, was taken by Dr. D. C. Garratt, F.R.I.C., Vice-President and Chairman of the Analytical Methods Committee of the Society for Analytical Chemistry. The meeting started with an Opening Address by the President of the Society for Analytical Chemistry, Mr. R. C. Chirnside, F.R.I.C., and was followed by "Fertiliser Analysis: A Decade of Collaborative Investigation," by J. H. Hamence, M.Sc., Ph.D., F.R.I.C. (read by J. C. Pinder, A.M.C.T., A.R.I.C., M.I.Chem.E.). Under the general heading "The Determination of Trace Elements in Fertilisers" the following papers were presented and discussed: "Introduction," by C. J. Regan, B.Sc., F.R.I.C.; "Determination of Molybdenum, Cobalt, Copper, Fluorine and Iodine," by R. F. Milton, B.Sc., Ph.D.,

M.I.Biol., F.R.I.C.; "Determination of Boron, Magnesium, Manganese and Zinc," by S. M. Boden, B.Sc., A.R.I.C.; "Determination of Iron, Chromium and Nickel," by J. B. E. Patterson, M.Sc., F.R.I.C.

The Chair at the second session, on the morning of April 22nd, was taken by Dr. G. W. Cooke, F.R.I.C., Member of the Council of the Fertiliser Society. The following papers were presented and discussed: "Determination of Nitrogen," by H. N. Wilson, F.R.I.C.; "Determination of Potassium," by E. W. Schwehr, B.Sc., and H. R. Conan, B.Sc., B.A., A.R.I.C.

At the final session, on the afternoon of April 22nd, the Chair was taken by Dr. B. Raistrick, M.I.Chem.E., F.R.S.E., Past President of the Fertiliser Society. The following paper was presented and discussed: "The Determination of the Phosphorus Content of Rock Phosphate," by H. L. Davies, B.Sc., Ph.D., J. Lacey, B.Sc., H. A. E. Mackenzie, B.Sc., Ph.D., A. Mendelowitz, M.Sc., Ph.D., M.S.A.Chem.I., and J. Rijkerr, D.Sc.

The meeting closed with Concluding Remarks made by Mr. J. Frisken, B.Sc., M.I.Chem.E., A.R.I.C., President of the Fertiliser Society.

NEW MEMBERS

Ordinary Members

Walter John Aley, B.Sc. (Lond.), A.R.I.C.; Keith Archer, B.Sc. (Lond.); Alan Baker, B.Sc. (Lond.), M.B.A.C.; Clarence Patrick Ball, A.R.I.C.; Mary Alice Birch, A.R.I.C.; Joseph Borg, Ph.C., L.P. (Malta), M.R.S.H.; Guillermo Carvajal-Sandoval; Brian Geoffrey Cooksby; Geoffrey Brian Crump, B.Sc. (Wales), A.R.I.C.; Michael Ellison; James Walker Blackie Erskine; Henry Albert Foner, B.Sc. (Leeds); Dennis Green; Ian Alfred Hansen, Ph.D. (Adelaide); James Arthur Hawes; Derrick Albert Hill, A.R.I.C.; Frederick John Howard, B.Sc. (Lond.); Peter Denzil Jones, A.R.I.C.; Brian Kerrigan; William Andrew Russell Macfarlane; Ronald Bruce Mutch, B.Sc. (Liv.); Raymond Edward Henry Rolfe; Guido Saini, Dr.Chem.; Rani Mahadeva Sastry, M.Sc. (Andhra); Peter William Shallis; Eric Ernest Ansell Styles, B.Sc. (Lond.); Geoffrey Morgan Telling; Alan Thompson, B.Sc. (Lond.), F.R.I.C., A.R.P.S.; Norman Victor West, B.Sc. (Lond.), A.M.I.S.P.; Frank Ronald Williams, B.Sc., Ph.D. (Lond.), F.R.I.C.

Junior Members

Ian Stephen Fox; Peter Anthony Hilling; Alan Godfrey Hudson, B.Sc. (Manc.).

DEATH

We record with regret the death of

Garfield Thomas.

NORTH OF ENGLAND SECTION

An Ordinary Meeting of the Section was held at 2.15 p.m. on Saturday, March 12th, 1960, at the "Nag's Head Hotel," Lloyd Street, Manchester. The Chair was taken by the Chairman of the Section, Dr. J. R. Edisbury.

The following paper was presented and discussed: "The Analysis of Non-soapy Detergent Products," by G. F. Longman, B.Sc., F.R.I.C.

SCOTTISH SECTION

An Ordinary Meeting of the Section was held at 7.15 p.m. on Friday, March 25th, 1960, at the Royal Society of Edinburgh, 22 George Street, Edinburgh, 2. The Chair was taken by Dr. Magnus A. Pyke, F.R.I.C., F.R.S.E., Vice-President of the Society.

The following paper was presented and discussed: "The Control of Quality in Synthetic Foodstuff Colours," by H. E. Stagg, B.Sc., F.R.I.C.

WESTERN SECTION

A Joint Meeting of the Section with the South Wales Section of the Royal Institute of Chemistry was held at 6.30 p.m. on Friday, March 11th, 1960, in the Department of Chemistry, University College, Singleton Park, Swansea. The Chair was taken by Mr. S. Dixon, M.Sc., F.R.I.C.

The following paper was presented and discussed: "Advantages and Disadvantages of Visual Colorimetry," by G. J. Chamberlin.

MIDLANDS SECTION

THE fifth Annual General Meeting of the Section was held at 7 p.m. on Wednesday, March 23rd, 1960, in the Nottingham and District Technical College, Burton Street, Nottingham. The Chair was taken by the Chairman of the Section, Dr. S. H. Jenkins, F.R.I.C., F.Inst.S.P. The following appointments were made for the ensuing year:—*Chairman*—Dr. S. H. Jenkins. *Vice-Chairman*—Dr. H. C. Smith. *Hon. Secretary*—Mr. G. W. Cherry, 48 George Frederick Road, Sutton Coldfield, Warwickshire. *Hon. Treasurer*—Mr. F. C. J. Poulton. *Hon. Assistant Secretary*—Mr. R. Adkins. *Members of Committee*—Mr. B. B. Bach, Dr. Bella B. Bauminger, Messrs. R. Belcher, W. E. Drinkwater, Miss C. J. Lloyd, Messrs. W. I. Stephen, W. H. Stephenson and M. Williams. Miss M. E. Tunnicliffe and Mr. J. Blenkin were appointed as Hon. Auditors.

MICROCHEMISTRY GROUP

THE twenty-fourth London Discussion Meeting of the Group was held at 6.30 p.m. on Wednesday, March 16th, 1960, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Vice-Chairman of the Group, Mr. C. Whalley, B.Sc., F.R.I.C.

A discussion on "Titrations in Non-aqueous Solvents," was opened by E. H. Tinley, B.Sc., F.P.S.

Annual Report of the Council: March, 1960

THE past year has seen steady progress in the many activities of the Society. The Sections and Groups have especially been active and a record number of meetings and joint meetings has been held. Society meetings also were varied and well attended. The Annual Conference of Honorary Secretaries of Sections and Groups was held on May 22nd, 1959. This Conference has become increasingly important in enabling the Honorary Secretaries to meet and to arrange Joint Meetings. This was particularly important this year as for the first time the Programmes Committee had become fully effective and was able to look ahead.

It is now nearly two years since the Programmes Committee, with Dr. J. Haslam as Chairman and Mr. L. Brealey as Secretary, began work, and the Society's current programme reflects the extent to which they have attempted to cover modern analytical methods and a wide variety of subjects. The scope of analysis is undoubtedly changing, and it is likely that the form of meeting required by members will also change. Much true analysis, particularly in the physical branches, is being performed by non-members of the Society, and with this in mind the programmes are being designed to attract to the Society analysts with as wide interests as possible. In particular, Council welcomes the requests that it has had from other learned Societies to hold joint scientific meetings. The calendar for the present session contains joint meetings with the Pharmaceutical Society in November; with the Oils and Fats Group of the Society of Chemical Industry; with the Fertiliser Society; and with the Fine Chemicals Group of the Society of Chemical Industry. The Society will also be holding Joint Symposia with the Institute of Metals and the Iron and Steel Institute in May, and in June with the Gas Chromatography Discussion Group in Edinburgh.

It is again a pleasure to comment on the increasing activities of the Sections and Groups. The Midlands Section has a very full programme and a Joint Symposium on "Food Analysis" with the Society was held in February at Birmingham. In response to an invitation from the Midlands Section, the Society is holding its Annual General Meeting for March, 1960, in Birmingham. The Council particularly welcomed this invitation and it is hoped that this Annual General Meeting will be followed by others outside London. The Scottish Section has also held an increased number of meetings, one of particular interest being held jointly with the Polarographic Society, in Belfast. A joint meeting with the North of England Section in Carlisle was also held.

The Analytical Methods Committee has been extending its work and the reports on Lonchocarpus, Rauwolfia and Capsaicin, jointly with the Pharmaceutical Society, formed the basis for a scientific meeting in November. Mr. S. C. Jolly has been appointed as part-time Publications Secretary for special publications outside the general scope of Committee and Panel reports.

Once again it has not been necessary to ask the Chemical Council for a grant towards the publication of the Society's journals, and for the second time the Society's publications have shown an excess of income over expenditure.

Council records with pleasure the award of the Nobel Prize to Professor J. Heyrovský and the award of the O.B.E. to Dr. R. T. Colgate. It congratulates Dr. R. Belcher on his appointment as first Professor of Analytical Chemistry at Birmingham University.

The Society now has 1941 members, an increase of 24 over the membership of a year ago.

LONG MEMBERSHIP—The congratulations and good wishes of the Council are extended to G. T. Bray, F. R. Dodd, R. C. H. Gilbard and F. W. G. King, who have completed 40 years of membership.

DEATHS—The Council regrets to have to record the deaths of the following members—

G. M. Bennett	R. S. Haskew	P. Murphy
A. Carey	E. W. Jackson	F. L. Okell
H. Dryerre	C. Lessner	E. Pedley
A. J. Durre	S. J. Lewis	C. A. Seyler
C. E. Gill	T. W. Lovett	G. R. Simpson
H. W. Harman	G. C. Matthews	A. W. Williams

SOCIETY MEETINGS—Eight meetings of the Society were held during the year and the following papers were read and discussed—

April, 1959, in London:

"A Modified Hydroxamic Acid Method for the Estimation of Total Esterified Fatty Acids in Plasma," by D. M. Morgan and K. J. Kingsbury, M.B., B.S., Ph.D.

"The Determination of Small Amounts of α-Picoline in Pyridine by a Solution-temperature Method," by K. A. Adey, B.Sc., F.R.I.C., and J. D. Cox, B.Sc., Ph.D., A.R.C.S.

"The Separation of Copper, Cobalt and Nickel," by W. D. Duffield.

"The Additive Effect of Substituent Groupings in the Chromatographic Behaviour of Phenoxy-acetic Acids," by L. S. Bark, B.Sc., F.R.I.C., and R. J. T. Graham, B.Sc.

May, 1959, in London, on the Design of Experiments in Analytical Chemistry:

"The Fundamental Principles of Modern Experiment Design," by E. C. Wood, B.Sc., Ph.D., A.R.C.S., F.R.I.C.

"Statistics in Standardising Chemical Methods," by W. C. Wake, M.Sc., Ph.D., F.I.R.I., F.R.I.C.

May, 1959, in London, special meeting on the Determination of Vitamin E; A Collaborative Study of Quantitative Paper Chromatography and the Development of a Recommended Method of Analysis. The speakers were:

A. L. Bacharach, M.A., F.R.I.C.
J. Green, B.Sc., Ph.D., F.R.I.C.
P. W. Russell Eggitt, B.Sc., Ph.D., F.R.I.C.
R. J. Ward, B.Sc., Ph.D., F.R.I.C.

October, 1959, in London, on Atmospheric Pollution Analysis:

"Analytical Aspect of the Control of Industrial Atmospheric Contamination," by J. C. Gage, B.Sc., Ph.D., F.R.I.C.

"The Determination of Beryllium Metal in Air," by R. J. Powell, B.Sc., P. J. Phennah and J. E. Still, B.Sc., F.R.I.C.

"The Determination of Atmospheric Polycyclic Hydrocarbons," by B. T. Commins, M.Sc., A.R.I.C.

November, 1959, in London:

"A Spectrographic Method for the Analysis of High-purity Acids," by J. H. Oldfield, F.R.I.C., and E. P. Bridge, B.Sc.

"The Colorimetric Micro-determination of Copper in Water: A Survey of Available Methods," by B. Tuck, B.Sc., A.R.I.C., and E. M. Osborn.

"Spectrofluorimetry of Lubricating Oils—Determination of Oil Mist in Air," by C. A. Parker, B.Sc., Ph.D., F.R.I.C., and W. J. Barnes.

November, 1959, in London, Joint Meeting with the Pharmaceutical Society on Methods of Assay of Capsicum, Lonchocarpus and Rauwolfia:

"Determination of Capsaicin in Capsicum and its Preparations," by H. B. Heath, M.B.E., B.Pharm., F.P.S.

"Determination of Rotenone in Lonchocarpus, Derris and their Extracts," by R. F. Phipers, B.Sc., Ph.D.

"Determination of Reserpine-type Alkaloids in Rauwolfia," by C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.

February, 1960, in London, Joint Meeting with the Oils and Fats Group of the Society of Chemical Industry:

"Spectroscopic Investigations of Fats," by D. Chapman, M.Sc., Ph.D.

February, 1960, in Birmingham, Symposium on "Food Analysis":

"Some Analytical Problems in the Dairy Industry," by K. A. Hyde, B.Sc., F.R.I.C.

"Routine Control in the Brewery," by W. A. Whitley, M.I.Biol.

"Control Tests in the Flour Milling Industry," by J. Williams, B.Sc., Ph.D., F.R.I.C.

"Quality Control Analysis of Pre-packed Foods," by G. Walley, B.Sc., F.R.I.C.

NORTH OF ENGLAND SECTION—The membership of the Section is 411, compared with 405 last year. The main centres of membership are: Merseyside 100, Manchester 70, North Lancashire and Cumberland 42, Tees-side 35, West Yorkshire 30, South Yorkshire 27 and East Yorkshire 27. Mr. L. R. Flynn was appointed Local Representative for the North-east Area of the Section at the Annual General Meeting.

During 1959, nine meetings have been held, including the usual Summer Meeting. The following papers were read and discussed—

Manchester, January, 1959, Annual General Meeting:

"Synthetic Foodstuff Colours—Control of Quality," by H. E. Stagg, B.Sc., F.R.I.C.

Leeds, March, 1959, jointly with the Association of Public Analysts:

Discussion on "The Composition of Milk," opened by J. Markland, B.Sc., F.R.I.C.

Liverpool, April, 1959:

"The Training of Analytical Chemists," by G. F. Longman, B.Sc., F.R.I.C., and J. W. Lucas, B.Sc., F.R.I.C.

Scarborough, June, 1959, Summer Meeting:

"Ice Cream," by K. Durham, B.Sc.

Carlisle, September, 1959, jointly with the Scottish Section:

"Determination of Water," by J. H. Thompson, B.Sc., Ph.D., A.R.I.C.

"Water Analysis as a Guide to Potability," by J. G. Sherratt, B.Sc., F.R.I.C.

"Determination of Radioactive Contaminants in Water," by G. E. Eden, B.Sc., A.R.I.C.

Sheffield, October, 1959, jointly with the Physical Methods Group and the Modern Methods of Analysis Group of the Sheffield Metallurgical Association:

"Coulometry in the Analysis of Metals," by G. Mattock, B.Sc., Ph.D., A.R.I.C.

"High Frequency Titration," by E. S. Lane, B.Sc., Ph.D., F.R.I.C.

Newcastle, October, 1959, jointly with the Physical Methods Group and the Newcastle upon Tyne and North East Coast Section of the Royal Institute of Chemistry:

"Instrumental Developments in X-ray Fluorescence Spectroscopy," by J. R. Stansfield, M.A., F.Inst.P.

"Some Applications of X-ray Spectrography," by H. I. Shalgosky, B.Sc., A.R.I.C.

Stockton-on-Tees, October, 1959:

"The Changing Aspects of Chemical Analysis," by H. N. Wilson, F.R.I.C.

Liverpool, December, 1959:

"The Analysis of Cocoa and Chocolate in Relation to Modern Manufacturing Methods," by B. W. E. Minifie, F.R.I.C., and C. Harris, F.R.I.C.

SCOTTISH SECTION—The twenty-fourth Annual General Meeting of the Section was held as usual in January, 1959, once again in Glasgow, and since then eight scientific meetings, widely varied in character, have been held. There has been an increased emphasis on Joint Meetings, all four of which have been very successful; the first of these, with the Polarographic

Society, was in the form of a one-day Symposium held in Queen's University, Belfast, when seven papers were presented and discussed. In September, a meeting in Carlisle, jointly with the North of England Section, was memorable, evoking such interest as to be worth repeating more often. Of the last two meetings, both in Glasgow, the first was held jointly with the Glasgow and West of Scotland Section of the Royal Institute of Chemistry, and the most recent one saw an innovation. This was the joining of the Society with the three Chartered Bodies in their usual combined meeting on the first Friday in December, the speaker being by tradition the Chairman of the previous evening's Ramsay Dinner, who this year was Mr. E. le Q. Herbert, President of the Royal Institute of Chemistry.

The remaining four Ordinary Meetings comprised two in Glasgow, one in Edinburgh, and one in Queen's College, Dundee, whose enthusiastic audience more than made up for the East Coast's numerically smaller S.A.C. support. Membership of the Section has decreased by 4 to 127.

A major effort during the year has been the preliminary organisation involved in the holding of the Third International Symposium on Gas Chromatography, in Edinburgh next June. This is a joint concern of the Gas Chromatography Discussion Group under the auspices of the Hydrocarbon Research Group of the Institute of Petroleum, and our own Society, and members of the Section have been active with regard to problems of catering, accommodation and social and entertainments programmes.

The following papers have been presented and discussed—

Glasgow, January, 1959, Annual General Meeting:

"The Identification of Artificial Colouring Matter in Food," by P. S. Hall, B.Sc., F.R.I.C.

Edinburgh, February, 1959:

"Recent Advances in the Analytical Chemistry of Plutonium," by F. J. Woodman, B.Sc., A.R.I.C.

Glasgow, March, 1959:

"The Estimation of Digestible Carbohydrates in Poultry Foods," by W. Bolton, D.Sc., F.R.I.C., F.R.S.E.

"A Review of 'Rapid Methods' of Silicate Analysis," by E. L. P. Mercy, Ph.D., D.I.C.

Glasgow, April, 1959:

"The Analytical Chemistry of Some of the Lower Phosphorus Oxyacids," by D. S. Payne, B.Sc., Ph.D., A.R.C.S., A.R.I.C.

"Qualitative Analysis by Solvent Extraction Methods," by R. A. Chalmers, B.Sc., Ph.D., and D. M. Dick, B.Sc.

Belfast, June, 1959, jointly with the Polarographic Society:

"The Polarographic Investigation of Some Copper Complexes in Non-aqueous Solution," by Z. P. Zagorski.

"Aspects of the Polarographic Behaviour of Rhenium and Technetium," by R. J. Magee, M.Sc., Ph.D., A.R.I.C.

"The Application of Polarography to Tissue Respiration," by I. S. Longmuir, M.B., B.Chir.

"Potentiometric Acid - Base Titrations in Acetone - Water Solutions of Nitrocellulose," by L. R. Leake and G. F. Reynolds, B.Sc., F.R.I.C.

"The Polarographic Determination of Nitroglycerine," by A. F. Williams, B.Sc., F.R.I.C.

"The Polarographic Behaviour of Metallic Ions in Molten Nitrates," by R. L. Faircloth, B.Sc., F.R.I.C.

"The Polarographic Estimation of Mercury Fulminate," by J. Hetman, A.R.I.C.

Carlisle, September, 1959, jointly with the North of England Section:

Details of the papers read at this meeting are given in the report of the North of England Section.

Dundee, October, 1959:

"Complexones, with Special Reference to EDTA," by H. J. Cluley, M.Sc., Ph.D., F.R.I.C.

Glasgow, November, 1959, jointly with the Glasgow and West of Scotland Section of the Royal Institute of Chemistry:

"Techniques in Radiochemistry for Analysis and Research," by D. A. Lambie, B.Sc., F.R.I.C.

Glasgow, December, 1959, jointly with the Chemical Society, the Glasgow Section of the Society of Chemical Industry and the Glasgow and West of Scotland Section of the Royal Insitute of Chemistry:

"Petroleum Refining: A Chemisc's View of To-day and To-morrow," by E. le Q. Herbert, B.Sc., F.H.-W.C., M.I.Chem.E., F.Inst.Pet., M.Inst.F., F.R.I.C.

WESTERN SECTION—The policy of holding joint meetings has again been continued. This undoubtedly makes for better attendances, although even then some have been rather poor, for example, that on December 11th, when the three Societies only attracted just over 30. It has also been the continued policy to hold meetings in as many parts of the Section as possible. This has the advantage that a good lecture can often be repeated in another part of the area, as, for example, the lecture by Mr. D. W. Wilson, which was originally given in Cardiff in December, 1958, and was then repeated in Swansea in March, 1959. Similarly, that of Mr. G. J. Chamberlin will be repeated in Swansea this session. The Summer Meeting in Poole was disappointing in that, owing to lack of support from Section members, a visit to The British Drug Houses Ltd., which had been arranged with some difficulty, had to be cancelled. The remainder of the meeting, however, was well supported, and Dr. James's lecture was very well received.

The membership of the Section shows a slight advance over that of last year and stands at 101.

The following papers have been presented and discussed—

February, 1959, Bristol, jointly with the Bristol Section of the Chemical Society:
"Some Aspects of Phosphorylation," by Professor Sir Alexander Todd, M.A., D.Phil., D.Sc., F.R.S.

March, 1959, Swansea, jointly with the South Wales Section of the Royal Institute of Chemistry:
"New Trends in Qualitative Analysis," by D. W. Wilson, M.Sc., F.R.I.C.

April, 1959, Salisbury, jointly with the Mid-Southern Counties Section of the Royal Institute of Chemistry:
"Advantages and Disadvantages of Visual Colorimetry," by G. J. Chamberlin.

May, 1959, Swansea, jointly with the Microchemistry Group, the South Wales Section of the Royal Institute of Chemistry and the University College of Swansea Chemical Society:
"Modern Methods of Silicate Rock Analysis," by R. A. Chalmers, B.Sc., Ph.D.
"Modern Trends in Geochemical Analysis," by E. A. Vincent, M.A., B.Sc., Ph.D., F.R.I.C.
"Geochemical Prospecting," by J. S. Webb, Ph.D., A.R.S.M., M.I.M.M.

June, 1959, Poole, jointly with the Poole and District Technical Group:
"The Work of the Public Analyst," by G. V. James, M.B.E., M.Sc., Ph.D., F.R.I.C.

October, 1959, Salisbury, jointly with the Mid-Southern Counties Section of the Royal Institute of Chemistry:
"Chemical Analysis and Clinical Diagnosis," by Professor Sir E. Charles Dodds, M.V.O., D.Sc., Ph.D., M.D., Hon.Sc.D., F.R.C.P., F.R.I.C., F.R.S.E., F.R.S.

December, 1959, Cardiff, jointly with the Cardiff and District Section of the Royal Institute of Chemistry and the South Wales Section of the Society of Chemical Industry:
"The Work of the Railway Chemist," by E. D. Henley, B.Sc., F.R.I.C.

MIDLANDS SECTION—The membership of the Section is 335, consisting of 302 ordinary members and 33 junior members. This is an increase of 9 ordinary members during the year.

Through the generosity of Mr. W. T. Elwell, Division Chief Analyst, Imperial Chemical Industries (Metals Division)Ltd., Birmingham, a member of the Midlands Section, the Section has inaugurated an annual competition for the best paper dealing with some aspect of analytical chemistry submitted by a young scientist, under the age of 30, working or residing in the Section's area. The award will be held for a year, and consists of a silver cigarette box inside the lid of which is a plaque formed by strips of titanium, zirconium, niobium and tantalum, all metals which are currently being developed for use in modern industry. Seven papers were submitted for the first year of the award and were assessed by Professor R. Belcher, Dr. D. C. Garratt and Mr. W. T. Elwell; the three finalists read their papers at a Section meeting on January 7th, 1960. The winner of the award for 1959 was announced at this meeting.

The average attendance at meetings was 40, with a maximum of 89 and a minimum of 26.

The following papers have been presented and discussed—

January, 1959, Birmingham:

Discussion on "The Analytical Chemistry of Cobalt and Nickel," opened by A. J. Brookes, A.R.I.C., A.C.T.

February, 1959, Birmingham, on Recent Advances in the Analytical Chemistry of Polymers:

"Infra-red and Near Infra-red Spectroscopy in the Analysis of Elastomers," by P. J. Corish, M.Sc.
"Ultra-violet Spectroscopy in the Analysis of Raw Materials and Compounded Rubbers," by D. W. Huke, B.Sc., and C. E. Kendall, B.Sc., A.R.I.C.

March, 1959, Birmingham:

Annual General Meeting.

March, 1959, Nottingham:

"The Microbiological Assay of the B Vitamins," by F. W. Norris, Ph.D., D.Sc., A.R.C.S., D.I.C.

March, 1959, Birmingham, jointly with the Physical Methods Group, on X-ray Fluorescence:

"Instrumental Developments in X-ray Fluorescence Spectroscopy," by J. R. Stansfield, M.A., F.Inst.P.
"Some Applications of X-ray Spectrography," by H. I. Shalgosky, B.Sc., A.R.I.C.

March, 1959, Birmingham:

"Some Aspects of the Analytical Applications of Chelate Compounds," by Professor H. Freiser.

April, 1959, Birmingham:

"Analytical Chemistry in Glass Manufacture," by J. Davies.

April, 1959, Nottingham:

"Quality Control in a Pharmaceutical Organisation," by D. C. Garratt, Ph.D., D.Sc. F.R.I.C.

May, 1959, Luton:

"The Analysis of Silicones and Related Organo-silicon Compounds," by J. C. B. Smith.

September, 1959, Birmingham:

Discussion on "Some Applications of EDTA," opened by T. S. West, B.Sc., Ph.D., A.R.I.C., J. Blenkin, B.Sc., and C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.

October, 1959, Coventry:

"The Analytical Chemistry of Tantalum and Niobium," by A. R. Powell, F.I.M., F.R.I.C., F.R.S.

October, 1959, Nottingham:

Discussion on "The Purity of Analytical Reagents," opened by J. T. Yardley, B.Sc., F.R.I.C.

November, 1959, Birmingham:

"The Identification and Determination of Phenols," by L. Barker, B.Sc., Ph.D., A.R.I.C

December, 1959, Wolverhampton:

Discussion on "The Determination of Trace Impurities in Metals," opened by B. Bagshawe, A.Met., and W. T. Elwell, F.R.I.C.

December, 1959, Nottingham:

Discussion on "Kjeldahl Nitrogen Determinations," opened by R. A. Savidge, A.R.I.C., and H. C. Wilkinson, M.Sc., F.R.I.C

MICROCHEMISTRY GROUP—The membership of the Group is now 689, an increase of 46 in the past year.

During 1959 three Ordinary Meetings of the Group were held: in London on February 20th (the Annual General Meeting of the Group followed by an Ordinary Meeting); in Swansea on May 8th (together with the Western Section and the South Wales Section of the Royal Institute of Chemistry and the University College of Swansea Chemical Society); and in Oxford on October 2nd (together with the Thames Valley Section of the Royal Institute of

Chemistry and the London Section of the Society of Chemical Industry). The following papers were read—

London:

Retiring Chairman's Address, by D. F. Phillips, F.R.I.C.

Swansea:

Details of the papers read at this meeting are given in the report on the Western Section.

Oxford:

"Quantitative Commonsense and the Chemist," by E. C. Wood, B.Sc., Ph.D., A.R.C.S., F.R.I.C.

Five informal discussion meetings were held in London. The following are the topics discussed, and the speakers who introduced them—

"The Determination of Small Quantities of Toxic Substances in the Atmosphere," introduced by J. C. Gage, B.Sc., Ph.D., F.R.I.C.
Review Meeting for reconsidering subjects previously discussed.
"The Micro-determination of Physical Constants," introduced by M. Sobotka.
"The Dumas Determination of Nitrogen," introduced by S. Bance, B.Sc., F.R.I.C., and Miss M. Corner, B.Sc., F.R.I.C.
"Applications of the Flask Combustion Method," introduced by Miss M. Corner, B.Sc., F.R.I.C., and C. B. Dennis.

The Committee met three times during the year. Sub-Committees dealing with Reagents and Standards in Microchemistry, and with Discussion Meetings, have also met.

PHYSICAL METHODS GROUP—During the past year the Group has held five Ordinary Meetings and a meeting for the Demonstration of Laboratory-grade Equipment. Two of the Ordinary Meetings were held in London and one each in Birmingham, Sheffield and Newcastle. The Birmingham meeting was held jointly with the Midlands Section, the Sheffield meeting jointly with the North of England Section and the Sheffield Metallurgical Association, and the Newcastle Meeting jointly with the North of England Section and the Newcastle upon Tyne and North East Coast Section of the Royal Institute of Chemistry. The Demonstration Meeting was held at the Brunel College of Technology, Acton; a list of the apparatus demonstrated is given in *The Analyst*, 1959, **84**, 405 (July issue). This meeting attracted a large number of visitors.

The Committee has appointed convenors for Advisory Panels on Nuclear Magnetic Resonance, Atomic-Absorption Spectroscopy and X-ray Fluorescence.

The number of Group members is now 750. This is an increase of 42 since the last Annual Report.

The following papers were read and discussed at the Ordinary Meetings of the Group—

Modern Methods of Purification—London, November, 1958:

"Preparative-scale Gas Chromatography," by C. R. Patrick, B.Sc., Ph.D., A.R.I.C.
"Some Aspects of the Practice of Zone Refining," by C. R. Veale, Ph.D., A.R.C.S., D.I.C., A.R.I.C.

The Analysis of Intact Samples—London, February, 1959:

"The Use of Beta and Gamma Absorption Methods in the Analysis of Intact Samples," by J. F. Cameron, B.Sc.
"The Use of Radioactive Isotopes in Simple X-ray Fluorescent Analysis," by C. E. Mellish, B.A., D.Phil.
"Analysis by Nuclear Magnetic Resonance Techniques," by D. J. Ferrett, M.A., D.Phil.

X-ray Fluorescence—Birmingham, March, 1959:

Details of the papers read at this meeting are given in the report on the Midlands Section.

Modern Methods of Titration—Sheffield, October, 1959:

Details of the papers read at this meeting are given in the report on the North of England Section.

X-ray Fluorescence—Newcastle, October, 1959:

Details of the papers read at this meeting are given in the report on the North of England Section.

BIOLOGICAL METHODS GROUP—The membership of the Group is now 310. This shows an increase of 17 during the year 1959.

The Group has held six meetings during the year. On December 9th, 1958, a Discussion Meeting held in "The Feathers" Restaurant after the Annual General Meeting was opened by the retiring Chairman of the Group, S. K. Kon, Ph.D., D.Sc., F.R.I.C. On the evening of May 5th, 1959, a visit was paid to the Brewery of Messrs. Courage & Barclay and on June 4th, 1959, members visited the Cooper Technical Bureau at Berkhamsted.

The following papers were read and discussed—

December, 1958, London:

Discussion on "Methodological Reminiscences," opened by S. K. Kon, Ph.D., D.Sc., F.R.I.C.

February, 1959, London, jointly with the Biometric Society:

"Factors Affecting χ^2 (Slope) in Insulin Assays Using the Mouse Convulsion Method," by J. V. Smart, B.Sc., and G. A. Stewart, B.Sc.

"The Use of a Range Method in Estimating Variance in Biological Assays," by V. J. Birkinshaw, F.P.S.

"Comparison of the Approximate with the more Refined Methods for Treating (2 + 2) Quantal Response Assays," by K. L. Smith, M.P.S.

April, 1959, London:

Discussion on "Problems of Recording and Communicating Technical Information in a Commercial Research Organisation," opened by P. D. Waterhouse, B.Sc.

October, 1959, London:

Discussion on "Routine Toxicity Tests in the Control of Pharmaceuticals," opened by P. Andrews, B.Sc.

ANALYTICAL METHODS COMMITTEE—During the year, the work of the Committee, its Sub-Committees and of the Joint Committee with the Pharmaceutical Society has shown increasing activity; although the number of Committees (20) remains much the same as last year, the number of Committee meetings in the 12-month period has risen from 61 to 89.

In addition to the annual report of the Committee, 6 Reports of Sub-Committees and Panels and the complete report by Mr. T. T. Gorsuch of his research work at Harwell as a Scholar of the Society have been published in *The Analyst*. A short paper on "The Stability of Rescinnamine in Solution," by one of the Panels of the Joint Committee with the Pharmaceutical Society, was published in *The Journal of Pharmacy and Pharmacology* in April. The reports published in *The Analyst* were—

"Radiochemical Investigations on the Recovery for Analysis of Trace Elements in Organic and Biological Materials," by T. T. Gorsuch (*March*).

"The Determination of Lead," by the Metallic Impurities in Organic Matter Sub-Committee (*March*).

"Notes on Perchloric Acid and its Handling in Analytical Work," by the Metallic Impurities in Organic Matter Sub-Committee (*April*).

"The Determination of Tocopherols in Oils, Foods and Feeding Stuffs," by the Vitamin-E Panel (*June*).

"The Determination of the Capsaicin Content of Capsicum and its Preparations," by the Joint Committee of the Pharmaceutical Society and the Society for Analytical Chemistry (*October*).

"The Determination of Rotenone in Rotenone-bearing Plants with Special Reference to Lonchocarpus," by the Joint Committee of the Pharmaceutical Society and the Society for Analytical Chemistry (*December*).

"Application of Gas - Liquid Chromatography to Essential Oil Analysis," by the Essential Oils Sub-Committee (*December*).

Reports of special investigational work sponsored by the Analytical Methods Committee have been prepared and are in the press. These are—

"The Determination of Trace Quantities of Silver in Trade Effluents," by T. B. Pierce (work carried out at Oxford under the supervision of Dr. H. Irving).

"Investigation into the Use of Bioassay for Pesticide Residues in Foodstuffs," by P. H. Needham.

The reports of two of the Panels of the Joint Committee with the Pharmaceutical Society mentioned above, together with a description of the work of a third Panel on the analysis

of Rauwolfia, not yet published, formed the basis of a joint evening meeting with the Pharmaceutical Society in November. All three Panels are continuing their investigations into the application of the recommended methods to additional preparations of the drugs.

Increased activity has been evident in all the Sub-Committees and Panels of the Analytical Methods Committee itself. The Sub-Committee on Additives in Animal Feeding Stuffs (whose establishment was reported in last year's Report of the Council) appointed 4 Panels at the beginning of the year to investigate the application of known methods (as established for the additives *per se*) to the analysis of feeding stuffs. These 4 Panels are dealing, respectively, with prophylactics, antibiotics and vitamins (divided between 2 Panels). A fifth Panel has recently been appointed to investigate the application of methods for synthetic hormones. The application of methods for determining trace elements in feeding stuffs is already under investigation by a separate Sub-Committee.

The report by Mr. P. H. Needham gives the results of a special survey sponsored by the Analytical Methods Committee (through the Pesticides Residues in Foodstuffs Sub-Committee) to ascertain the extent to which bioassays are being used in the United Kingdom and abroad for the qualitative and quantitative examination of toxic residues. The results of this survey show that a systematic investigation for the development of bioassay methods as rapid "sorting" tests would be well worth while.

The report by Mr. T. B. Pierce on the determination of trace quantities of silver in trade effluents was the outcome of another special investigation sponsored by the Analytical Methods Committee, arising out of the work of the Joint Committee of the Society for Analytical Chemistry and the Association of British Chemical Manufacturers, whose collection of Recommended Methods for the Analysis of Trade Effluents was published as a book in 1958.

The 5 years' investigational work of the Vitamin-E Panel, published as a Report in June, was the subject of a special meeting of the Society in May.

Following the lead of the Society, the Analytical Methods Committee held a special meeting, to which all Chairmen of Sub-Committees were invited, to survey the work of the Committee as a whole and to discuss items of mutual interest. This proved to be a great success and similar meetings will be held annually.

As in other years, a separate Report giving full details of the work of the Committee during the year is being prepared and will be circulated to all contributors to the Analytical Methods Trust Fund.

LIAISON WITH OTHER SCIENTIFIC ORGANISATIONS—During the year the following appointments were made—

Joint Library Committee, Chemical Society:

Dr. J. G. A. Griffiths was again appointed the Society's representative.

British Iron and Steel Research Association:

Mr. R. C. Chirnside and Dr. J. Haslam represented the Society at the Thirteenth Chemists' Conference of the Methods of Analysis Committee (Metallurgy, General Division).

Parliamentary and Scientific Committee:

Mr. G. Taylor, who had represented the Society for many years, resigned and Dr. J. H. Hamence was appointed in his place.

Royal Institute of Chemistry, Summer School Organising Committee:

Dr. J. Haslam and Mr. C. Whalley.

Chemical Council:

Dr. R. E. Stuckey, who had represented the Society for the three-year period, was replaced by Dr. A. J. Amos.

B.S.I. Committees:

Mr. H. W. Hodgson, Chromatographic Analysis of Gases.
Miss M. Olliver, Gelatine.

The Council of the Society thanks all its representatives for the work they have carried out in the various Committees and at varied meetings during the year.

HONORARY TREASURER'S REPORT—The Society's income from members' subscriptions was greater by £150 than the corresponding figure for 1958, whereas expenditure exclusive of that allocated to publications and reserves exceeded that of the preceding year by £825. However, this deficit of £675 was covered eight times by the greatly enhanced excess of income over expenditure on the two Publications Accounts, the strong position of these accounts, despite an increase in publication expenses of over £4000, being due to the increased prices of the Journals to non-members. Accordingly, the over-all picture presented by the Society's General Income and Expenditure Account is an excess of income over expenditure nearly five times that of the previous year in spite of a total increase in expenditure of over £4500 and a considerably increased allocation to reserves. This outcome of the year's activities justifies a confident outlook on the future even although administration and publication costs have already risen substantially.

Following the amendments to the Memorandum of Association approved at an Extraordinary General Meeting early in 1959, representation was again made to the Commissioners of Inland Revenue for the Society to be recognised as a charity. The appeal was successful and the Society has been granted exemption from income tax.

PROGRAMMES COMMITTEE—During the past year the Programmes Committee organised eight Society meetings, seven of them in London and one in Birmingham. Continuing the policy of the previous year, two of the meetings were devoted to the presentation of papers that had been submitted for publication in *The Analyst*. These meetings do not always attract a good attendance, but the Committee feels that they should be continued for the time being in order to provide an occasional platform both for important new work and for young authors who otherwise might not get the opportunity to speak in public. Two meetings were held jointly with other learned Societies, one with the Pharmaceutical Society, when the work of three of the Joint Committees investigating methods of analysis of natural drugs was presented, and the other with the Oils and Fats Group of the Society of Chemical Industry. Another meeting was devoted to the reporting of the work of the Vitamin-E Panel of the Analytical Methods Committee. The Committee is anxious to provide a programme that caters for as many members of the Society as possible, and also to establish closer contacts with other learned bodies; to these ends it is its policy to continue to hold meetings outside London so that contact can be made with those members who find it difficult to travel to London and to arrange joint meetings and symposia with other groups. Three such symposia are being arranged in 1960, the first in April with the Fertiliser Society on the subject of "Fertiliser Analysis," the second in May with the Iron and Steel Institute and the Institute of Metals on "Determination of Gases in Metals," and the third during June with the Gas Chromatography Discussion Group of the Institute of Petroleum Hydrocarbon Research Group on "Gas Chromatography."

THE ANALYST—The Council of the Society has realised for quite a long time that the subject matter of many of the lectures and discussions at meetings, particularly of the Sections and Groups, was not reported in full in *The Analyst*, from want of either novelty or originality, and yet was of use to analysts; and it has been concerned to see if a way could be found for the Society to undertake the publication of such material.

A Sub-Committee of the Publication Committee was appointed for this purpose during the year and, after considering all aspects of the matter, it duly reported to the Publication Committee, and the report was sent in due course to the Council.

As a result it has been decided not to expand the scope of *The Analyst* itself, or to put papers now considered as unsuitable for *The Analyst* in the Bulletin; nor was it thought feasible to start a new journal for such material, as cost alone precluded this, and it was also thought that there were not enough papers to support a journal of this sort. It was decided, however, that papers of special merit which would not normally appear in *The Analyst* should be published as separate monographs, and that such papers might be invited if it were wished. The Bulletin may be expanded somewhat by including further news items.

The 1959 volume of *The Analyst* contained 756 pages, compared with 708 in 1958. The numbers of papers and notes published in 1959 were 89 and 52, respectively, against 86 and 53 in 1958. The Publication Committee's vigorous policy of collecting critical Review Papers has borne fruit, and six such papers were published during the year (they are included

in the totals). In addition, the Report of the Society's First Analytical Chemistry Research Scholar was published in the March number.

The average length of papers and notes (excluding this Report and the Review Papers) is 3·8 pages, an improvement on the previous year's 4·2. Shorter papers are not only economical in production costs: the more concisely scientific matter is presented, the more attractive it is to the reader, whose time is a scarce commodity, too. Our contributors' continuing efforts in this direction are most encouraging, and we are confident that the trend will continue.

The loss of six weeks' printing production in the summer as a result of a dispute involving the whole trade caused some delays, but our printers' strenuous efforts during the autumn brought the journal back on time-table for the December issue. Some reduction in the size of issues was necessary until November, but in the final analysis, nearly 15 per cent. more material was published than in the previous year. A steady increase also in the number of advertisers is indicative of *The Analyst*'s increasing value as a medium for commercial announcements. The number of copies of each issue being printed is now 6600.

Summaries of 21 papers presented at meetings but not being published in full anywhere were printed in the Proceedings of the Society.

Twelve issues of the Bulletin were distributed with *The Analyst* during the year. Special issues included one listing publications of analytical interest added during 1958 to the Chemical Society Library, which members of our Society have the privilege of using. An innovation in the March and April issues was the publication of news photographs, the latter issue containing an illustrated account of the Biennial Dinner. The amount of general information and news, both of forthcoming meetings and Symposia and of events that have taken place, is increasing, so that the Bulletin must inevitably grow in size and frequency of issue. Bulletins do not appear every month; in 1959 two issues appeared in each of the months April and May, and none in August and September. Apart from the more obvious case of a Special number, there are occasions when it is a technical advantage to produce two numbers in one month.

ANALYTICAL ABSTRACTS—In 1959 the total number of abstracts published was 5073, occupying 692 pages, an increase of 660 abstracts and 127 pages over 1958; this was achieved in spite of the delay caused by the printing dispute, which necessitated producing smaller monthly numbers in order to bring the date of publication back to normal with the December issue.

Early in the year the increasing number of abstracts made an increase of staff necessary and Dr. R. E. Essery was appointed as an editorial assistant. His long experience of analytical chemistry and of abstracting has been most helpful and, had it not been for the printing dispute, the arrears of abstracts would have been substantially reduced.

On the retirement of Dr. L. MacIntyre, Dr. H. F. W. Kirkpatrick was appointed to the Committee.

On December 3rd a meeting of abstractors was held at 14 Belgrave Square at which the Officers of the Society and members of the Abstracts Committee were present. Twenty-two abstractors attended. After a welcome by the President and Mr. B. A. Ellis, Chairman of the Abstracts Committee, the Editor addressed the meeting, pointing out some of the difficulties of the editorial staff and indicating ways in which abstractors could help. A very useful discussion followed.

R. C. CHIRNSIDE, *President.*

R. E. STUCKEY, *Honorary Secretary.*

Report of the Analytical Methods Committee 1959

THIS fifth Report of the Analytical Methods Committee of The Society for Analytical Chemistry reviews the progress of work during the twelve months ending February 29th, 1960.

GENERAL REVIEW

In April, 1959, the Committee was sorry to lose Mr. T. MacLachlan, through resignation; at the same time he relinquished his office as Chairman of the Metallic Impurities in Organic Matter Sub-Committee, but is continuing as a member of that committee. This opportunity is taken to thank him for all the help and guidance he has given to both committees.

PROGRESS OF WORK—

It is now five years since the Council of the Society decided to reorganise its Analytical Methods Committee (which has been in existence since 1924) with wider terms of reference, and to establish it as a financially independent unit with a permanent paid secretariat, in order to enable it to undertake the amount of work with which it was faced. This step was made possible by the very generous help given by Industry in response to an appeal for funds made by the Council in 1954, and continued annual donations by a number of organisations have permitted the work of the Committee to go forward with increasing vigour from year to year.

The progress of work in technical committees is inevitably somewhat slow; however, the Analytical Methods Committee has been able to maintain a steady output of reports. In 1955, the first of the methods for the analysis of trade effluents was nearing completion; these methods were prepared by the four panels of the Joint Committee of the Society (represented by the Analytical Methods Committee) and the Association of British Chemical Manufacturers, which had started its work early in 1954. During 1956, a number of these methods were published in *The Analyst*, as also was a Report on the determination of vitamin B_{12}, prepared by a Panel of the A.M.C. The year 1957 saw the publication of many more of the methods for trade effluents as well as two Reports from A.M.C. Sub-Committees; in 1958 the Society published in book form a comprehensive collection of all the methods for trade effluents.

The disbandment of the Joint Committee and its Panels did not mean any slackening in the pace of committee work, because a new Joint Committee, this time with The Pharmaceutical Society of Great Britain, with its five Panels, had been vigorously at work since its appointment in 1956. The Analytical Methods Committee had also appointed new Sub-Committees and Panels from time to time, so that the total had risen from 7 in 1955 to 13 in 1958, even after allowing for the disbandment of two Panels on the completion of their work.

This increase in committee work is shown more by an increase in the frequency of committee meetings than in their numbers: in 1958, when there was a total of 20 committees, the number of meetings was 72, whereas in 1959, the number of meetings was 91, although the committee total had only risen by 1.

This activity has resulted in the publication during 1959 of 6 reports by Sub-Committees and Panels. In addition, 3 more reports have been completed and publication is expected shortly. In the press, also, are 2 reports of individual work carried out at the request of, and financed by, the A.M.C.—in each case, the work was of a specialised nature, which, although arising from committee work, was unsuitable for a collaborative undertaking. The titles of the published reports are given in full, with their literature references, at the beginning of this Report,* but a brief mention of each, as well as of the completed (but as yet unpublished) reports, is made below.

Of the A.M.C. Sub-Committees, that on Metallic Impurities in Organic Matter has had a particularly fruitful year, with two reports already published: (*a*) on The Determination

* Not included in the text reproduced here—*Editor*.

of Lead and (*b*) Notes on Perchloric Acid and its Handling in Analytical Work—and two more just completed. These last two reports are (*a*) on The Determination of Small Amounts of Arsenic, which is in two parts, namely, a revision of the standard Gutzeit method (first published in 1930) and a recommended procedure by the molybdenum-blue method and (*b*) a systematic collection of established methods for the destruction of organic matter, with advice as to their use and their advantages and disadvantages in particular circumstances.

Last year's Annual Report mentioned the imminent publication of a special report of work carried out by the Society's research scholar, Mr. T. T. Gorsuch. His work, on the use of radiochemical techniques to investigate the recovery of trace elements from organic materials, stemmed directly from the difficulties encountered by the Metallic Impurities in Organic Matter Sub-Committee. Mr. Gorsuch's report was published in March, 1959.

Another imminent publication mentioned in last year's Report was that prepared by the Vitamin-E Panel on The Determination of Tocopherols in Oils, Foods and Feeding Stuffs. This was published in June, 1959, and in the previous month various members of the Panel gave an account of their work at a special meeting of the Society, because of its interest in being what is almost certainly the first collaborative study of two-dimensional paper chromatography as a procedure in quantitative analytical chemistry.

The Essential Oils Sub-Committee has been making practical use of the advantages of gas - liquid chromatography in elucidating the mechanisms of certain complex chemical reactions: the widely used method of hot formylation for the assay of citronellol in essential oils has from time to time given results slightly higher than theoretical, and various modifications have been proposed to remedy this defect. By the application of gas - liquid chromatography, the Sub-Committee showed clearly that substances other than citronellyl formate were produced, which, by the chemical method, were estimated as such. These findings are given in a interim report published by the Sub-Committee in December, but the Sub-Committee foresees that considerable work will be necessary before a precise method of determination can be devised.

The assay of crude drugs, for which there are no official or standard methods at present in force, is the concern of the Joint Committee of the Society with The Pharmaceutical Society, and here again there has been a successful year's work. Three of its Panels have completed their original programmes and two of these have already published their reports: (*a*) on The Determination of the Capsaicin Content of Capsicum and its Preparations and (*b*) on The Determination of Rotenone in Rotenone-bearing Plants with Special Reference to Lonchocarpus. The first report recommends a specific method after several had been investigated by the Panel. The method recommended in the second report is one that has been in commercial use over a number of years but which, because of its empirical nature, had been found to give different results in different laboratories: the Panel concerned found that precise definition of procedural detail and the introduction of a preliminary "cleaning-up" stage has resulted in a method that can now be used in different laboratories with a good degree of reproducibility. The need for attention to precise definition of procedure is becoming more and more apparent to other technical committees, also, as their work proceeds.

The third Panel of the Joint Committee, on methods for the assay of rauwolfia, has not yet published its final report. However, in the course of its work, the Panel had to investigate the effect of daylight on the stability of rescinnamine in solution, a subject which, although not analytical in itself, had a bearing on a method it considered might be of possible use. The Panel's findings, showing that deterioration occurred, were published as a separate report in the *Journal of Pharmacy and Pharmacology* in April.

Mention has been made earlier (p. 318) of individual work commissioned by the A.M.C. In addition to the report of work by Mr. Gorsuch, which has been published, 2 other special reports giving accounts of individual investigations are in the press. One of these, by Mr. T. B. Pierce,* under the direction of Dr. H. Irving at Oxford, was mentioned in last year's Annual Report as being near publication, but this was delayed because of a need to clarify certain points. This investigation, on devising a method for determining traces of silver in trade effluents, arose from the work of the Joint Committee mentioned previously. Although silver is an unlikely contaminant because of its economic value, it is nevertheless extremely toxic to fish, and, in the event of its accidental release into rivers, it was considered that a sensitive method for its determination would be necessary.

* This has appeared since the date of this Annual Report (*Analyst*, 1960, **85**, 166; March).

The second special report is by Mr. P. H. Needham, of Rothamsted Experimental Station, on the extent to which bioassays are used as a rapid means of detecting or determining toxic pesticide residues in food. This investigation arose from the deliberations of the Pesticides Residues in Foodstuffs Sub-Committee, and it was suggested that the work of devising a rapid "sorting test" might well be delegated to a research worker appointed by the Society. However, before a decision was made on such a step, Mr. Needham was appointed to make a review of the literature and of any practical applications of bioassay methods in industrial laboratories, in the hope of discovering some indication of a basic set of conditions that could be used in the development of a standard method. It was found that a number of laboratories, both in Britain and on the Continent, are using such methods, but mostly these are of an *ad hoc* nature to suit particular requirements. The Committee decided that the publication of this preliminary report would be of considerable interest and that it might well provide a stimulus for systematic research on a larger scale than was at first envisaged.

Another aspect of the Committee's activities is the collection and systematic publication in book form of all recommended methods published by the Committee to date: in addition, the "Bibliography of Standard Methods of Analysis," published in 1951, requires review and expansion to bring it up to date. In last year's Report, mention was made of the decision of the Committee to appoint a Publications Secretary for this purpose, since the existing committee work on the preparation of new methods did not leave any time for the present secretariat to devote to this extra editorial work.

The Committee is pleased, therefore, to announce that Mr. S. C. Jolly has been appointed on a part-time basis to carry out this work, under the direction of a special Publications Sub-Committee.

The other Sub-Committees and Panels have continued to make progress during the year, and details of their personnel and reports of work will be found on pp. 320 to 330. Of these, two are Panels that have been recently appointed—one, on methods for synthetic hormones, in connection with the work of the Additives in Animal Feeding Stuffs Sub-Committee, was appointed at the end of 1958, and the other, on methods for the assay of pyrethrum, in connection with the work of the Joint Committee on Methods for the Assay of Crude Drugs.

ANALYTICAL METHODS TRUST—

The number of industrial organisations that gave donations to the Trust Fund during the year was 32, the total amount received being £4857. This represents a decrease of 13 in the number of subscribers and a decrease of approximately £540 in subscriptions, as compared with 1958.

INCOME AND EXPENDITURE—

The statement of accounts (see Appendix I) for the financial year ending October 31st, 1959, shows an expenditure of £4170 and a gross income of £5462. Expenditure is only slightly higher than in 1958: although the amount spent on salaries was higher owing to an increase in staff, the amount for grants for special investigations was much less than in the previous year.

REPORTS OF SUB-COMMITTEES OF THE ANALYTICAL METHODS COMMITTEE

ADDITIVES IN ANIMAL FEEDING STUFFS SUB-COMMITTEE

CONSTITUTION—

D. C. Garratt, Ph.D., D.Sc., F.R.I.C. (*Chairman*)	*Boots Pure Drug Co. Ltd.*
A. J. Amos, B.Sc., Ph.D., F.R.I.C.	*Analytical and Consulting Chemist.*
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
R. F. Phipers, B.Sc., Ph.D.	*The Cooper Technical Bureau*
S. A. Price, B.Sc., F.R.I.C.	*Vitamins Ltd.*
C. J. Regan, B.Sc., F.R.I.C.	Formerly *Chemist-in-Chief, London County Council*
W. L. Sheppard, F.R.I.C.	*Unilever Ltd.*
R. E. Stuckey, Ph.D., D.Sc., F.P.S., F.R.I.C.	*British Drug Houses Ltd.*
F. R. Williams	*Ministry of Agriculture, Fisheries and Food*
Miss C. H. Tinker (*Secretary*)	

TERMS OF REFERENCE—"To investigate and prepare methods for determining the amounts of additives (nutrients, stimulants and prophylactics) in animal and poultry feeding stuffs."

PROGRESS OF WORK—

This Sub-Committee, which acts in a steering capacity, was appointed at the end of 1958, in response to a request from the Scientific Sub-Committee of the Standing Advisory Committee, Fertilisers and Feeding Stuffs Act, 1926, of the Ministry of Agriculture, Fisheries and Food for advice on the availability of suitable methods of analysis for the various types of additives commonly included in animal and poultry feeding stuffs. The additives concerned fell into five principal groups—antibiotics, synthetic hormones, minerals, prophylactics and vitamins—and on this basis the detailed work of investigating suitable methods was assigned to a number of working panels, the vitamins group being sub-divided between two panels, based on the distinction between "fat-soluble" and "water-soluble" vitamins. Since a Sub-Committee was already in existence engaged in the investigation of methods for trace elements in fertilisers and animal feeding stuffs (see p. 326), it undertook to act also as the Minerals Panel.

The growing practice of adding to animal feeding stuffs, not only vitamins and nutritional supplements, but also drugs and medicaments for the stimulation of growth and control of disease, set new problems in analysis and control. A particular feature of this development is the need to bring together the specialised knowledge of two hitherto unrelated fields of analytical activity—that of the pharmaceutical industry on the one hand and of the animal-feeding-stuffs industry on the other—and it has been necessary to bear this important aspect in mind when appointing Panels for the investigation of methods.

It soon became apparent at the start of each of the new working panels' deliberations that not only would the supplemented feed (as fed to the animal) have to be considered, but also the higher-potency preparations that are supplied as diet supplements, either for intimate admixture by the feeding-stuff supplier or for individual administration by the user. Although methods do exist (published or unpublished) for most, if not all, of the substances *per se* used as additives, in very few instances has it been established that such methods can be applied to the determination of those substances when present in feeds: to a lesser extent, this also applies to the high-potency preparations. Broadly speaking, there are three factors to be taken into account when applying a method to feeds; these are—

(*a*) the much lower level of concentration of the additive in question (a factor that affects the sensitivity of a method);

(*b*) the interference of the ingredients of the basic feed;

(*c*) the interference of other additives (in some instances, the identity of these may not be known to the analyst).

Details of the work of each of the Panels are given below, but it should be mentioned here that the representative sampling of feeding stuffs (although this question does not strictly come within the purview of this Sub-Committee's work) is of considerable importance because of the low levels of concentration of additives usually encountered. In order to investigate the precision of any proposed method, each panel has prepared special samples, and experience has shown that extreme care is required in the admixture of the additives and that the degree of fineness of milling can be critical in ensuring the production of a uniformly mixed sample for analytical purposes.

ANTIBIOTICS PANEL

CONSTITUTION—

S. A. Price, B.Sc., F.R.I.C. (*Chairman*)	*Vitamins Ltd.*
A. J. Cavell, M.Sc., A.R.C.S., D.I.C., F.R.I.C.	*Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service*
O. Hughes	*Pfizer Ltd.*
W. P. Jones, F.P.S., F.R.I.C.	*Cyanamid of Great Britain Ltd., Lederle Laboratories.*
J. S. Simpson, F.I.M.L.T.	*Glaxo Laboratories Ltd.*
Miss J. Stephens, B.Sc.	*Distillers Co. Ltd.*
G. Sykes, M.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
Miss A. M. Parry (*Secretary*)	

PROGRESS OF WORK—

Collaborative trials have shown that each of the three antibiotics, penicillin, aureomycin and oxytetracycline, can be assayed in pre-mixes by either chemical or microbiological methods. At the low levels at which the antibiotics are added to feeding stuffs, chemical methods are not applicable, and microbiological methods are being examined with a view to unifying the varied techniques of assay at present in use and devising satisfactory methods of extraction from the feeding stuff.

HORMONES PANEL

CONSTITUTION—

R. E. Stuckey, Ph.D., D.Sc., F.P.S., F.R.I.C. (*Chairman*)	*British Drug Houses Ltd.*
J. Allen, A.R.I.C.	*British Drug Houses Ltd.*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
W. L. Sheppard, F.R.I.C.	*Unilever Ltd.*
Miss A. M. Parry (*Secretary*)	

PROGRESS OF WORK—

The Panel has been examining methods for the determination of stilboestrol and hexoestrol in feeding stuffs and has concentrated on chemical methods for the determination of these substances after extraction and isolation from the material. A collaborative trial has given encouraging results, but it has been found that attention to detail is necessary to obtain complete recovery.

PROPHYLACTICS PANEL

CONSTITUTION—

R. F. Phipers, B.Sc., Ph.D. (*Chairman*)	*The Cooper Technical Bureau*
C. W. Ballard, B.Sc., F.P.S., F.R.I.C.	*May & Baker Ltd.*
N. C. Brown, M.A., B.Sc., A.R.I.C.	*The Cooper Technical Bureau*
H. G. Dickenson, B.Sc., Ph.D.	*Ward, Blenkinsop & Co. Ltd.*
A. W. Hartley, F.R.I.C.	*Spillers Ltd.*
A. Holbrook, F.R.I.C.	*Imperial Chemical Industries Ltd. (Pharmaceutical Division)*
S. G. E. Stevens, B.Sc., F.R.I.C.	*Smith Kline & French Laboratories Ltd.*
Miss A. M. Parry (*Secretary*)	

PROGRESS OF WORK—

Although chemical methods are available for most of the coccidiostats and anti-blackhead drugs with which the Panel is concerned, collaborative tests have revealed the need for modification in order to deal with interfering substances present in feeding stuffs. These difficulties have now been resolved in the method for nitrofurazone, and progress is being made on the method for sulphaquinoxaline. The Panel is considering methods for the isolation and identification of the three sulpha drugs (sulphaquinoxaline, sulphaguanidine and sulphadimidine).

In addition to the drugs listed in the original remit to the Panel, any new products that may become more widely used are being noted and will be investigated if necessary.

VITAMINS (FAT-SOLUBLE) PANEL

CONSTITUTION—

W. L. Sheppard, F.R.I.C. (*Chairman*)	*Unilever Ltd.*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
C. R. Louden, B.Sc., F.R.I.C.	*R. Silcock & Sons Ltd.*
H. Pritchard, M.Sc., F.R.I.C.	*Analytical and Consulting Chemist*
R. A. Rabnott	*Analytical and Consulting Chemist*
S. A. Reed, B.Sc., A.R.I.C.	*The British Cod Liver Oil Co.*
G. Walley, B.Sc., F.R.I.C.	*Unilever Ltd.*
J. Williams, B.Sc., Ph.D., F.R.I.C.	*Spillers Ltd.*
D. R. Wraige, B.Sc., A.R.I.C.	*J. & H. Robinson Ltd.*
Miss C. H. Tinker (*Secretary*)	

PROGRESS OF WORK—

The vitamins assigned to this Panel were vitamin A, β-carotene and vitamin D. Since there are no chemical methods available for vitamin D, the official chick method, which measures the anti-rachitic activity of the vitamin, was accepted.

Spectrophotometric methods for the determination of vitamin A and for β-carotene have been investigated by the Panel, and collaborative tests have indicated that these are satisfactory when applied to most types of feeding stuffs, provided that strict attention is paid to the details of the saponification and extraction techniques. The incorporation in feeds of beads of protected vitamin A necessitates the achievement of a well mixed sample for analysis.

VITAMINS (WATER-SOLUBLE) PANEL

CONSTITUTION—

A. J. Amos, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Analytical and Consulting Chemist*
B. M. Gibbs, B.Sc., A.R.I.C.	*Unilever Ltd.*
S. A. Price, B.Sc., F.R.I.C.	*Vitamins Ltd.*
H. Pritchard, M.Sc., F.R.I.C.	*Analytical and Consulting Chemi*
F. Clermont Scott, B.Sc., F.R.I.C.	*Vitamins Ltd.*
J. S. Simpson, F.I.M.L.T.	*Glaxo Laboratories Ltd.*
G. Sykes, M.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd*
J. Williams, B.Sc., Ph.D., F.R.I.C.	*Spillers Ltd.*
Miss C. H. Tinker (*Secretary*)	

PROGRESS OF WORK—

The water-soluble vitamins being investigated by the Panel belong to the B group. Attention has been confined to the investigation of microbiological methods because of their sensitivity and specificity in view of the low concentrations of added vitamins in feeding stuffs. Collaborative tests have proved that the standard microbiological methods for the assay of riboflavin and pyridoxin are not applicable to enriched feeds, and independent research into these methods is under investigation.

Preliminary collaborative tests on the assay of nicotinic acid and vitamin B_{12} have given more encouraging results, but further tests are required.

CHLORINE IN ORGANIC COMPOUNDS SUB-COMMITTEE

CONSTITUTION—

Professor R. Belcher, Ph.D., D.Sc., F.Inst.F., F.R.I.C. (*Chairman*)	*University of Birmingham (Departme Chemistry)*
J. H. Dunn, B.Sc., A.R.I.C.	*Plant Protection Ltd.*
K. Gardner, B.Sc., F.R.I.C.	*Fisons Pest Control Ltd.*
R. Goulden, A.R.I.C.	*"Shell" Research Ltd.*
G. Ingram, A.R.I.C.	*Courtaulds Ltd.*
C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.	*Boots Pure Drug Co. Ltd.*
Miss A. M. G. Macdonald, M.Sc., Ph.D., A.R.I.C.	*University of Birmingham (Department of Chemistry)*
Miss C. H. Tinker (*Secretary*)	

TERMS OF REFERENCE—"To prepare methods for the determination of organically-bound chlorine, having special reference to commercial preparations such as pesticides."

PROGRESS OF WORK—

The Sub-Committee has been investigating the application of the oxygen-flask (sometimes known as the Schöniger-flask) method on the semi-micro scale to the determination of chlorine in technical grades of pesticides and in solid and liquid formulations.

After a number of modifications to the apparatus and technique, the method appears to be satisfactory for products containing not less than 10 per cent. of organically-bound chlorine. However, difficulty has been experienced in trying to apply the technique to the analysis of low-concentrate dusts, owing to the presence of a relatively large amount of inorganic filler, and the problem is still being investigated.

ESSENTIAL OILS SUB-COMMITTEE

CONSTITUTION—

G. W. Ferguson, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Analytical and Consulting Chemist*
A. J. M. Bailey, B.Sc., F.P.S., F.R.I.C.	*W. J. Bush & Co. Ltd.*
D. Holness, B.A.	*Unilever Ltd.*
H. T. Islip, B.Sc., F.R.I.C.	Formerly *D.S.I.R., Tropical Products Institute*
P. McGregor, B.Sc., A.H.-W.C., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
T. L. Parkinson, B.Sc., Ph.D., F.R.I.C.	*Beecham Foods Ltd.*

G. B. Pickering, B.Sc., Ph.D.	*D.S.I.R., Tropical Products Institute*
J. H. Seager, M.Sc., F.R.I.C.	*Yardley & Co. Ltd.*
G. E. Smith, B.Sc., F.R.I.C.	*Stafford Allen & Sons Ltd.*
S. G. E. Stevens, B.Sc., F.R.I.C.	*Smith Kline & French Laboratories Ltd.*
B. D. Sully, B.Sc., Ph.D., A.R.C.S., F.R.I.C.	*A. Boake, Roberts & Co. Ltd.*
Miss C. H. Tinker (*Secretary*)	

PROGRESS OF WORK—

As mentioned earlier in this Report (see p. 319), the Sub-Committee has published an interim report on the unsuitability of hot formylation methods for determining citronellol in essential oils, as demonstrated by the application of gas - liquid chromatography for studying the course of the chemical reactions. It is hoped that it will be possible to devise an alternative to the formylation methods that have been in use for many years; a method in which gas - liquid chromatography is used would be a possibility provided that a suitable internal standard can be found.

The investigation into the efficiency of drying agents for essential oils has now been completed and a report is being prepared.

Work is proceeding on the search for a suitable method for the determination of phenols, since the present alkali-absorption method is not specific: in this connection, methods involving titration in non-aqueous solvents are being examined. Work is also proceeding on methods for determining carbonyl compounds.

The traditional method for assaying geraniol in citronella oil has been to determine the "total acetylisables," but it has been recognised for some time that this value is a complex characteristic that may give rise to misleading inferences in certain cases. Various modifications are being examined, with different acylating agents, with a view to finding one that will be specific for the alcohol.

MEAT PRODUCTS SUB-COMMITTEE

CONSTITUTION—

S. M. Herschdoerfer, Ph.D., F.R.I.C. (*Chairman*)	*T. Wall & Sons Ltd.*
S. Back, B.Sc., F.R.I.C.	*Crosse & Blackwell Ltd.*
Miss E. M. Chatt, B.Sc., F.R.I.C.	*British Food Manufacturing Industries Research Association*
P. O. Dennis, B.Sc., F.R.I.C.	*Oxo Ltd.*
C. D. Essex, A.M.Inst.B.E., F.R.I.C.	*Liebig's Extract of Meat Co. Ltd.*
J. R. Fraser, B.Sc., A.C.G.F.C., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
R. A. Lawrie, B.Sc., Ph.D., F.R.I.C.	*A.R.C., Low Temperature Research Station*
E. F. Williams, M.A., F.R.I.C. (*deputy* H. C. Hornsey, F.R.I.C.)	*J. Sainsbury Ltd.*
H. Amphlett Williams, Ph.D., A.C.G.F.C., F.R.I.C.	*Public Analyst*
Miss C. H. Tinker (*Secretary*)	

TERMS OF REFERENCE—"(*a*) The determination of the meat content of products containing meat; (*b*) the determination of the constituents of meat and meat products.

NOTE—The term 'meat products' to include hydrolysed protein and, if found necessary, fish pastes."

PROGRESS OF WORK—

When the Sub-Committee was reconstituted in 1955, the alternative methods for the determination of meat content of manufactured products were reviewed—namely, that of Stubbs and More in which the nitrogen content is determined, and that of Osman Jones based on the determination of starch content. Preference was expressed for the former method, but, in view of the evidence that the nitrogen factors published by Stubbs and More in 1919 were not altogether valid for present-day use, the Sub-Committee has concerned itself with the re-assessment of those factors.

For this purpose, it was necessary to acquire as much information as possible on the analysis of meat, both of whole carcases and of individual cuts. This proved to be a lengthy task, during the course of which various meat-product manufacturers and meat research organisations in this country and abroad were approached. In view of the difficulties of obtaining full details, the Sub-Committee finally decided to concentrate its attention on the nitrogen content of pork in the first instance, and to base its findings mainly on a particular series of specially planned experiments carried out in one laboratory.

As a result, an interim report has now been prepared on nitrogen factors for pork, and this will shortly be published.

Meanwhile, the Sub-Committee is proceeding on similar lines to collect figures for beef and veal. The question of the correction for cereal filler in meat products is also under consideration.

METALLIC IMPURITIES IN ORGANIC MATTER SUB-COMMITTEE

CONSTITUTION—

W. C. Johnson, M.B.E., F.R.I.C. (*Chairman*)	*Hopkin & Williams Ltd.*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
Miss E. M. Chatt, B.Sc., F.R.I.C.	*British Food Manufacturing Industries Research Association*
J. C. Gage, B.Sc., Ph.D., F.R.I.C.	*Imperial Chemical Industries Ltd. (Industrial Hygiene Laboratories)*
T. T. Gorsuch, B.Sc., A.R.I.C.	*U.K. Atomic Energy Authority, The Radiochemical Centre*
E. I. Johnson, M.Sc., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
T. McLachlan, D.C.M., A.C.G.F.C., M.I.Biol., F.R.I.C.	*Public Analyst*
R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.	*Analytical and Consulting Biochemist*
G. E. Willis, B.Sc., Ph.D., A.R.I.C.	*Imperial Chemical Industries Ltd. (Dyestuffs Division)*
Miss A. M. Parry (*Secretary*)	

TERMS OF REFERENCE—"To investigate the determination of small quantities of metals in organic matter."

PROGRESS OF WORK—

During the past year two reports from the Sub-Committee have been published in *The Analyst*, namely, "The Determination of Lead" (March), and "Notes on Perchloric Acid and its Handling in Analytical Work" (April). The latter has since been reprinted in Swedish.

The Sub-Committee has completed its work on arsenic, and its report, to be published shortly, includes both the molybdenum-blue and the Gutzeit methods; the latter has been revised in accordance with present practice and supersedes the earlier S.P.A. Report (*Analyst*, 1930, **55**, 102).

Since the destruction of organic matter is a necessary preliminary in the analysis of all samples being considered by the Sub-Committee, this aspect of its work has been treated as the subject of a separate report containing a collection of methods for both wet and dry combustion. This report, which will be published shortly, will be referred to in subsequent reports on the determination of trace metals, but should, in addition, prove useful to analysts generally.

The Sub-Committee has now turned its attention to methods for the determination of copper and mercury.

Close liaison is being maintained between this Sub-Committee and the Trace Elements in Fertilisers and Feeding-stuffs Sub-Committee.

DIRECT MICRO-DETERMINATION OF OXYGEN IN ORGANIC MATTER SUB-COMMITTEE

CONSTITUTION—

D. W. Wilson, M.Sc., F.R.I.C. (*Chairman*)	*Sir John Cass College (Department of Chemistry)*
P. R. W. Baker, B.Sc., A.R.I.C.	*Wellcome Research Laboratories*
Miss B. B. Bauminger, Ph.D., A.I.R.I., F.R.I.C.	*Dunlop Research Centre*
W. T. Chambers, B.Sc., Ph.D., A.R.I.C.	*British Rubber Producers' Research Association*
A. F. Colson, B.Sc., Ph.D., F.R.I.C.	*Imperial Chemical Industries Ltd. (Alkali Division)*
Miss M. Corner, B.Sc., F.R.I.C.	*D.S.I.R., National Chemical Laboratory*
Miss J. Cuckney	*Imperial College of Science and Technology (Department of Chemistry)*
F. Ellington, B.Sc., A.R.C.S., F.R.I.C.	*National Coal Board, Central Research Establishment,*
G. Ingram, A.R.I.C.	*Courtaulds Ltd.*
F. J. McMurray	*Wellcome Chemical Works*
M. P. Mendoza, B.Sc., A.R.C.S.	*British Coal Utilisation Research Association*
F. H. Oliver	*Parke, Davis & Co. Ltd.*
H. J. Warlow	*D.S.I.R., Tropical Products Institute*
C. Whalley, B.Sc., F.R.I.C.	*Laporte Chemicals Ltd.*
Miss C. H. Tinker (*Secretary*)	

TERMS OF REFERENCE—"To investigate the Unterzaucher method, and its modifications, for the micro-determination of oxygen."

PROGRESS OF WORK—

In the first two series of collaborative tests, the Sub-Committee put samples of varying oxygen content through the whole combustion train. Consideration of the results of these tests indicated that it was impossible to ascertain at which particular stage of the procedure a cause could be found for the discrepant results that were obtained, and the fact that laboratories have from time to time introduced modifications to their apparatus also complicated the issue.

The Sub-Committee has now decided to turn its attention to separate stages and, in the first instance, is investigating the end reaction—*i.e.*, that of pure carbon monoxide with iodine pentoxide—and tests are proceeding on these lines.

PESTICIDES RESIDUES IN FOODSTUFFS SUB-COMMITTEE

CONSTITUTION—

R. A. E. Galley, B.Sc., Ph.D., A.R.C.S., D.I.C., F.R.I.C. (*Chairman*)	*D.S.I.R., Tropical Products Institute*
G. L. Baldit, B.Sc., A.R.I.C.	*Plant Protection Ltd.*
B. A. Ellis, O.B.E., M.A., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
J. C. Gage, B.Sc., Ph.D., F.R.I.C.	*Imperial Chemical Industries Ltd. (Industrial Hygiene Laboratories)*
D. C. Garratt, Ph.D., D.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
G. S. Hartley, D.Sc.	*Research Centre of Fisons Pest Control Ltd.*
C. O. Harvey, B.Sc., A.R.C.S., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
J. G. Reynolds, F.Inst.Pet., F.R.I.C.	*"Shell" Research Ltd.*
G. Taylor, O.B.E., F.R.I.C.*	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
Miss C. H. Tinker (*Secretary*)	

* Since deceased.

TERMS OF REFERENCE—"To consider the analytical problems that arise, or may arise, in connection with the presence of pesticide residues in foodstuffs; and to advise as to analytical procedures for the detection and determination of any such residues or their breakdown products."

PROGRESS OF WORK—

The Sub-Committee's principal consideration during the year has been the problem of the need for rapid "sorting" tests for detecting the presence of residues in toxic amounts. Most of the chemical methods at present available take a considerable time to perform, mainly because of the need to identify, in many instances, the suspected contaminant and then to extract it from the plant material, the constituents of which frequently interfere with the chemical determination. This need for reduction in the time taken for assay is particularly important to the Public Analyst, when perishable foods are concerned.

As mentioned earlier in this Report (see p. 320), the investigation carried out by Mr. P. H. Needham, on the extent to which bioassays are being used in this country as a rapid means of detecting and determining toxic residues, was commissioned at the request of the Sub-Committee as a first step in trying to resolve the problem.

TRACE ELEMENTS IN FERTILISIERS AND FEEDING-STUFFS SUB-COMMITTEE

CONSTITUTION—

C. J. Regan, B.Sc., F.R.I.C. (*Chairman*)	Formerly *Chemist-in-Chief, London County Council*
S. M. Boden, B.Sc., A.R.I.C.	*Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
S. G. Burgess, B.Sc., Ph.D., F.Inst.Pet., M.Inst.S.P., F.R.I.C.	*London County Council*
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
E. I. Johnson, M.Sc., F.R.I.C.	*D.S.I.R., Laboratory of the Government Chemist*
R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.	*Analytical and Consulting Biochemist*
R. L. Mitchell, B.Sc., Ph.D., F.R.S.E., F.R.I.C.	*Macaulay Institute for Soil Research*
J. B. E. Patterson, M.Sc., F.R.I.C.	*Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service*
W. L. Sheppard, F.R.I.C.	*Unilever Ltd.*
J. Williams, B.Sc., Ph.D., F.R.I.C.	*Spillers Ltd.*
Miss C. H. Tinker (*Secretary*)	

TERMS OF REFERENCE—"To devise appropriate methods of analysis (to be recommended for inclusion in the Regulations under the Fertilisers and Feeding Stuffs Act, 1926) for the determination of boron, cobalt, copper, fluorine, iodine, iron, magnesium, manganese, molybdenum, selenium and zinc, which can be expected to be present in fertilisers and feeding stuffs.

PROGRESS OF WORK—

Methods for 10 of the 11 elements mentioned above have been agreed upon. Difficulty is being experienced in the search for a chemical method for determining trace amounts of selenium in feeding stuffs: this element is definitely toxic at 0·1 p.p.m., and a method should be capable of determining it down to 0·01 p.p.m.

Cognisance has been taken of the methods (under revision) given in the Regulations under the Fertilisers and Feeding Stuffs Act, 1926, and when applicable, those methods are accepted.

In addition to the 11 elements listed in the original Terms of Reference, the Sub-Committee is to recommend methods for chromium and nickel, which may be present in fertilisers if sewage sludges are used: a method for calcium in feeding stuffs is also to be recommended.

For those trace elements present in fertilisers as well as in feeding stuffs, the Sub-Committee has endeavoured, so far as is possible, to recommend methods that can be applied to both types of material. In general, chemical methods are given, but, in some instances, spectrographic or flame-photometric methods are also given when these are considered to be more accurate.

As mentioned earlier (see p. 321), this Sub-Committee acts as the Minerals Panel of the Additives in Animal Feeding Stuffs Sub-Committee.

REPORT OF THE P.S. - S.A.C. JOINT COMMITTEE ON METHODS OF ASSAY OF CRUDE DRUGS

MAIN COMMITTEE

CONSTITUTION—

Representing the Pharmaceutical Society of Great Britain—	
K. R. Capper, Ph.D., B.Pharm., F.P.S., D.I.C. (*Chairman*)	*Pharmaceutical Society of Great Britain*
J. W. Fairbairn, B.Sc., Ph.D., F.P.S., F.L.S. F.R.I.C.	*University of London (School of Pharmacy)*
R. Higson, F.P.S.	*Ministry of Health, Supplies Division*
W. Mitchell, B.Sc., Ph.D., F.R.I.C.	*Stafford Allen & Sons Ltd.*
R. E. Stuckey, Ph.D., D.Sc., F.P.S., F.R.I.C.	*British Drug Houses Ltd.*
Representing the Society for Analytical Chemistry—	
C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.	*Boots Pure Drug Co. Ltd.*
H. C. Macfarlane, A.R.T.C.S., F.R.I.C.	*Analytical and Consulting Chemist*
D. Watt, F.P.S.	*T. & H. Smith Ltd.*
D. C. Garratt, Ph.D., D.Sc., F.R.I.C. (*ex-officio*)	*Chairman of the Analytical Methods Committee*
Representing the Tropical Products Institute, D.S.I.R.—	
A. J. Feuell, B.Sc., Ph.D., A.R.I.C.	
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C. (*Secretary*)	*Secretary to the Analytical Methods Committee*
Miss A. M. Parry, B.Sc. (*Assistant Secretary*)	*Assistant Secretary to the Analytical Methods Committee*

TERMS OF REFERENCE—"To prepare standard methods of assay of crude drugs and kindred materials."

PROGRESS OF WORK—

Mention has been made earlier in this Report (see p. 319) of the completion of work by three of the Panels of the Joint Committee, leading to the publication, in October and December, of reports from two of those Panels; the report from the third Panel has been approved for publication and it should appear in *The Analyst* within the next few months.

A new Panel, the sixth to be appointed since the Joint Committee started its work in March, 1956, has been set up to investigate methods for pyrethrum.

Individual reports from each of the Panels are given below.

Panel 1: *Digitalis purpurea*—chemical method

Constitution—

Professor H. Brindle, M.Sc., F.P.S., F.R.I.C. (*Chairman*)	*Emeritus Professor of Pharmacy, University of Manchester*
G. E. Foster, B.Sc., Ph.D., F.R.I.C.	*Wellcome Chemical Works*
G. J. Rigby, M.Sc., Ph.D., Dip.Bact.	*University of Manchester (Department of Pharmacy)*
K. L. Smith, M.P.S.	*Boots Pure Drug Co. Ltd.*
Professor J. P. Todd, Ph.D., F.P.S., F.R.I.C.	*Royal College of Science and Technology, Glasgow (School of Pharmacy)*
W. D. Williams, B.Pharm., Ph.D., F.P.S., A.R.I.C.	*Royal College of Science and Technology, Glasgow (School of Pharmacy)*
Miss A. M. Parry (*Secretary*)	

Terms of reference—"To investigate chemical methods for the assay of digitalis and its preparations and to attempt to correlate them with the biological method of assay."

Progress of work—

In an attempt to correlate the results of chemical methods of assay of digitalis with those obtained by biological means, the Panel has based its work on the examination of two samples of *Digitalis purpurea* leaf, known to have widely different biological activities. Preliminary chemical tests, with three different reagents, yielded good inter-laboratory agreement, but the values for the total glycosides, calculated as digitoxin, were very different for each of the three reagents and showed no correlation with results obtained by biological assay.

Further tests, in which an attempt was made to separate the active glycosides from the inactive ones, revealed that more information as to the main constituents of the leaf and their relative biological activities would be required before a satisfactory chemical method of assay could be devised. The work, both chemical and biological, necessary to obtain this information is more suited to individual research than to collaborative work by a Panel, and research on these lines is being undertaken at the University of Manchester. Meanwhile the Panel has suspended its activities, but it is hoped that, when the results of further research are available, it will be possible to propose a procedure for collaborative trial by the Panel.

Panel 2: Capsicum—capsaicin content

Constitution—

H. B. Heath, M.B.E., B.Pharm., F.P.S. (*Chairman*)	*Stafford Allen & Sons Ltd.*
E. A. Elsbury, F.R.I.C.	*Parke, Davies & Co. Ltd.*
Miss B. M. Luckett	*W. J. Bush & Co. Ltd.*
C. A. MacDonald, B.Sc., F.R.I.C.	*The Evans Medical Research Laboratories*
G. R. A. Short, F.P.S.	*W. J. Bush & Co. Ltd.*
D. O. Singleton, B.Sc.	*Beecham Maclean Ltd.*
Miss G. M. Wells, B.Sc., A.P.I.	*Beecham Maclean Ltd.*
A. J. Woodgate, B.Sc.	*Stafford Allen & Sons Ltd.*
Miss A. M. Parry (*Secretary*)	

Terms of reference—"To investigate methods of assay of capsicum and capsicum products with particular reference to the determination of the capsaicin content."

Progress of work—

The Panel's report on "The Determination of the Capsaicin Content of Capsicum and its Preparations," published in the October issue of *The Analyst*, deals with the chemical assay of capsicums having a relatively high capsaicin content, the oleoresin and some of the British Pharmaceutical Codex preparations.

Work is now in progress on the modification of the method for the assay of capsicum in wool and in ointments, and on methods for distinguishing between pure capsaicin and the synthetic capsaicins that are used in some formulated products.

Panel 3: Anthraquinone drugs

Constitution—

W. Mitchell, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Stafford Allen & Sons Ltd.*
J. W. Fairbairn, B.Sc., Ph.D., F.P.S., F.L.S., F.R.I.C.	*University of London (School of Pharmacy)*

C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.	*Boots Pure Drug Co. Ltd.*
S. C. Jolly, B.Sc., B.Pharm., F.P.S., A.R.I.C.	*Pharmaceutical Society of Great Britain*
Miss H. M. Perry, M.Sc., F.R.I.C.	*Stafford Allen & Sons Ltd.*
H. A. Ryan, B.Sc., F.R.I.C.	*Westminster Laboratories Ltd.*
W. Smith, B.Sc., F.R.I.C.	*Allen & Hanburys Ltd.*
R. V. Swann, B.Sc., F.R.I.C.	*Allen & Hanburys Ltd.*
Miss A. M. Parry (*Secretary*)	

TERMS OF REFERENCE—"To investigate methods for estimating the purgative activity of drugs and preparations of drugs containing anthraquinone derivatives with a view to recommending standard methods of assay."

PROGRESS OF WORK—

Work has continued on the determination of the sennoside content of a number of samples of Alexandrian and Tinnevelly senna pods by a chemical colorimetric method of assay and on the assessment of the activity of the same samples by biological methods.

PANEL 4: RAUWOLFIA

CONSTITUTION—

C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C. (*Chairman*)	*Boots Pure Drug Co. Ltd.*
T. Davies, B.Sc., A.R.I.C.	*CIBA Laboratories Ltd.*
Miss B. Gartside, B.Pharm.	*Pharmaceutical Society of Great Britain*
J. J. Lewis, M.Sc., F.P.S.	*University of Glasgow (Department of Materia Medica and Therapeutics)*
A. W. Peacock, B.Pharm., F.P.S.	*Riker Laboratories Ltd.*
Miss A. M. Parry (*Secretary*)	

TERMS OF REFERENCE—"To investigate methods of assay for rauwolfia and its preparations with particular regard to the content of reserpine and related alkaloids."

PROGRESS OF WORK—

As mentioned in the introduction to this Report (p. 319), a report by the Panel on the effect of daylight on solutions of rescinnamine was published in the April issue of the *Journal of Pharmacy and Pharmacology*.

The Panel has now completed its work on a colorimetric method for the determination of reserpine-like alkaloids in rauwolfia and its extracts, and the report will be published shortly, after which the Panel will be disbanded.

PANEL 5: LONCHOCARPUS AND DERRIS

CONSTITUTION—

R. F. Phipers, B.Sc., Ph.D. (*Chairman*)	*The Cooper Technical Bureau*
R. Buckley, B.Sc., A.R.I.C.	*Plant Protection Ltd.*
J. A. Dawson, B.Sc., A.R.I.C.	*D.S.I.R., Tropical Products Institute*
W. E. Drinkwater, F.R.I.C.	*Boots Pure Drug Co. Ltd.*
R. V. Foster, M.Sc., A.R.I.C.	*The Cooper Technical Bureau*
S. C. Jolly, B.Sc., B.Pharm., F.P.S., A.R.I.C.	*Pharmaceutical Society of Great Britain*
J. T. Martin, B.Sc., D.Sc., F.R.I.C.	*University of Bristol (Long Ashton Research Station)*
R. A. Rabnott	*Analytical and Consulting Chemist*
D. V. Richmond, B.Sc.	*University of Bristol (Long Ashton Research Station)*
F. H. Tresadern	*Stafford Allen & Sons Ltd.*
Miss A. M. Parry (*Secretary*)	

TERMS OF REFERENCE—"To investigate methods of assay of derris, lonchocarpus and their preparations, with particular reference to the determination of their rotenone content."

PROGRESS OF WORK—

As mentioned in the introduction to this Report (p. 319), the Panel's report on "The Determination of Rotenone in Rotenone-bearing Plants with Special Reference to Lonchocarpus" was published in the December issue of *The Analyst*.

The gravimetric method, given in the above report, is not applicable to many preparations, owing to interferences or the low rotenone content of the sample. The Panel is, therefore, carrying out investigations in an attempt to improve the reproducibility of results by colorimetric methods, which, though they may not give an accurate figure for the true rotenone content of the sample, are suitable for the control of commercial preparations containing rotenone.

Panel 6: Pyrethrum

Constitution—

W. Mitchell, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Stafford Allen & Sons Ltd.*
H. E. Coomber, B.Sc.	*Mitchell Cotts & Co. Ltd.*
L. Donegan	*D.S.I.R., Tropical Products Institute*
M. Elliott, Ph.D.	*Rothamsted Experimental Station*
A. D. Harford	*British Petroleum Research Station*
S. C. Jolly, B.Sc., B.Pharm., F.P.S., A.R.I.C.	*Pharmaceutical Society of Great Britain*
W. S. Manson, B.Sc., A.R.I.C.	*The Cooper Technical Bureau*
R. A. Rabnott	*Analytical and Consulting Chemist*
F. H. Tresadern	*Stafford Allen & Sons Ltd.*
T. F. West, Ph.D., D.Sc., A.M.I.Chem.E., F.R.I.C.	*African Pyrethrum Technical Information Centre Ltd.*
Miss A. M. Parry (*Secretary*)	

Terms of reference—"To investigate methods of assay of pyrethrum flowers and pyrethrum extract with a view to recommending a standard chemical or physical method of assay."

The first meeting of this Panel was held on February 9th, 1960, when the programme of work was discussed.

APPENDIX I

The Society for Analytical Chemistry Analytical Methods Trust Accounts for the Year Ended October 31st, 1959

Income and Expenditure Account for the Year Ended October 31st, 1959

1958		£	£	*1958*		£
£	£			£		
	Rent, Light, Heat and			*5394*	Subscriptions from Industry ..	4857
222	Telephone	314		*10*	Interest from Investments (gross) ..	10
2785	Salaries	3140		*622*	Bank Deposit Interest	360
119	Office Equipment ..	115			Grant from Society for Analytical Chemistry for work done on "Recommended Methods for the	
222	Printing and Stationery	266				
12	Travelling Expenses ..	23				
76	Expenses of Meetings ..	65		—	Analysis of Trade Effluents" ..	235
21	Audit Fee	21				
105	Postage and Petty Expenses	119				
3562			4063			
524	Scholarship Grants and Awards for Research		107			
1940	Excess of Income over Expenditure for the year ended October 31st, 1959, transferred to Accumulated Fund		1292			
£6026			£5462	£6026		£5462

Accumulated Fund

1958			*1958*		
£		£	£		£
12,794	Balance carried to Balance Sheet	14,086	*10,854*	Balance at October 31st, 1958 ..	12,794
			1940	Excess of Income over Expenditure for the year ended October 31st, 1959	1292
£12,794		£14,086	£12,794		£14,086

Balance Sheet at October 31st, 1959

1958			1958				
£		£	£	£		£	£
	Accumulated Fund:				*Investments (at Cost):*		
12,794	Balance at October 31st, 1959	14,086			£100 Ceylon Government 3½% Stock, 1934–59	61	
121	*Sundry Creditors*	3,264		61			
					£100 3½% Conversion Stock	83	
				83			
				100	£100 3½% War Stock	100	
				244			244
					(Market Value at 31.10.59, £217)		
			169		*Sundry Debtors* ..		22
					Cash at Banks:		
				7000	On Deposit Account	9000	
				5502	On Current Account	8084	
			12,502				17,084
£12,915		£17,350	£12,915				£17,350

Signed on behalf of the Analytical Methods Trust Fund G. H. LLOYD-JACOB, *Chairman*,
J. HUBERT HAMENCE, *Honorary Treasurer*.

Report of the Auditors to the Trustees of The Society for Analytical Chemistry Analytical Methods Trust Fund

We have examined the above Balance Sheet which in our opinion gives a true and fair view of the state of affairs of the Trust at 31st October, 1959.

10 New Court,
Lincoln's Inn,
LONDON, W.C.2.
29th March, 1960.

(Signed) RIDLEY, HESLOP & SAINER,
Chartered Accountants,
Auditors.

APPENDIX II

SUBSCRIBERS TO THE TRUST FUND DURING 1959

Albright & Wilson Ltd.
Associated Ethyl Co. Ltd.
Boots Pure Drug Co. Ltd.
The British Aluminium Co. Ltd.
The British Drug Houses Ltd.
British Oxygen Research & Development Ltd.
Brotherton & Co. Ltd.
Cadbury Brothers Ltd.
Central Electricity Generating Board
The Distillers Co. Ltd.
Dunlop Rubber Co. Ltd.
Esso Research Ltd.
Glaxo Laboratories Ltd.
Arthur Guinness, Son & Co. (Park Royal) Ltd.
H. J. Heinz Co. Ltd.
Hopkin & Williams Ltd.
Huntley & Palmers Ltd.
Imperial Chemical Industries Ltd.
Laporte Chemicals Ltd.
J. Lyons & Co. Ltd.
Macfarlane, Lang & Co. Ltd.
May & Baker Ltd.
The Metal Box Co. Ltd.
The Millers' Mutual Association
Procea Products Ltd.
Quaker Oats Ltd.
Rowntree & Co. Ltd.
"Shell" Research Ltd.
John & E. Sturge Ltd.
Unilever Ltd.
Vitamins Ltd.
Weston Research Laboratories Ltd.

The Sixth Bernard Dyer Memorial Lecture

Chemical Analysis and Medical Progress

By A. C. FRAZER

(*Delivered after the Annual General Meeting of the Society, March 2nd, 1960*)

I GREATLY appreciate the honour of being invited to deliver the Sixth Bernard Dyer Memorial Lecture. I am also deeply conscious of the fact that there are many people in the Midlands who are much better qualified than I to discharge this important task. Nevertheless, there are certain aspects of the life and work of Bernard Dyer that lead me to hope that my remarks this evening will not be entirely inappropriate to the occasion.

I did not have the privilege of personal friendship with Bernard Dyer, but his pioneer work in the field of agricultural chemistry is, of course, well known to everyone. The first Memorial Lecturer, Sir John Russell,[1] gave a clear picture of the man, and each successive Memorial Lecturer[2,3,4,5] has chosen some facet of Bernard Dyer's many interests and activities as the basis for his lecture. The features in the story of Bernard Dyer's life that strike me most forcibly are his devotion to the cause of making analytical chemistry an effective tool in an applied field, his intense practicality and his ability to understand the needs of people with a different background, training and experience and, in turn, to be understood and appreciated by them.

In choosing the subject for this Sixth Memorial Lecture I was tempted to speak on various food problems with which I have been associated for some years, and there is no doubt that some of these would have been of direct interest to Bernard Dyer. However, this field had already been covered to some extent by Hughes[3] in the Third Memorial Lecture in 1954. In view of this and the special features of Bernard Dyer's work that had particularly caught my attention, it seemed to me that it might not be inappropriate to give some consideration in the Sixth Memorial Lecture to the application of chemical analysis to another vast field of scientific endeavour—Medicine. It is, of course, impossible to consider more than a small part of this subject in the time available. One approach might have been to review the highlights of medical discovery and examine the contributions made by chemical analysis. As everyone here knows, chemical analysis often provided the essential stepping-stones leading to great and far-reaching exploration and discovery. However, I did not feel that this was the right approach on this occasion. I have, therefore, decided to put before you a series of practical problems encountered almost daily by my colleagues and myself in the course of our medical researches. These will illustrate the sort of difficulties, often involving chemical analysis, that may arise, not only in medical research, but in daily practice. Many of them are still not fully solved. They call for a closer understanding between groups of people with different backgrounds, training and experience. My preoccupation with our own particular problems is not because I think they are in any way unique, but, on the contrary, because they will serve to illustrate many common issues. They are representative of day-to-day practical problems, which, in another field, used to delight the heart of the man whose memory we are here to honour.

The problems that I propose to put before you have arisen in the course of detailed studies carried out by my colleagues and myself over a number of years on a group of patients with defective absorption from the small intestine. These patients commonly present with loss of weight, signs and symptoms of nutritional deficiency, and steatorrhoea. Steatorrhoea means the passage of bulky, fluid or semifluid, pale, offensive, fatty stools. The long-term objective of this work is to contribute to new knowledge of the physiology of the human small intestine, a vital organ without which life cannot be maintained indefinitely. The more immediate objective of these studies has been to determine, if possible, the different causes of the absorptive fault; to devise effective methods of differentiating between the various types of the syndrome and to evolve rational treatment directed towards correction of the causative defect.

The first step in the study of any syndrome or symptom complex is to choose one feature as an anchor; a sign or symptom that may be taken as an essential feature for diagnostic

purposes and that will give some guide to improvement or aggravation of the patient's condition. Clearly, the sign or symptom chosen should be one that can be quantitatively assessed without great difficulty. In the group of patients with which we are concerned various features might be selected. For example, body weight might be used. However, in some of these patients, there may be a severe reduction of plasma proteins and this may lead to oedema or water-logging of the tissues; under such circumstances, body weight is no longer a useful guide to the nutritional status of the patient. It is, therefore, an unsuitable index in this group. Body height is another possibility, but this is only affected in growing children, and not in all cases, even in this group. We have, therefore, chosen as our anchor the amount of long-chain fatty acids in the stools. This is relatively easily measured and has proved to be a useful guide to the general condition of the patient. Other features of the stool, especially its volatile-fatty-acid and nitrogen contents, may be usefully measured at the same time.

It used to be the practice to estimate the percentage of fat in a small stool sample; this is seldom done to-day. It is a thoroughly unsatisfactory method, since a small and irrelevant change in the diet, such as a change from white to brown bread, will alter the residue in the stools and profoundly affect the fat percentage. More recently a fat-balance technique has been advocated[6] in which the fat intake and fat output are carefully measured over a suitable experimental period of five to ten days. This is still the method of choice under certain circumstances, especially if the fat intake is low or extremely variable. In the majority of patients, however, it is not necessary to measure the fat intake accurately in order to diagnose steatorrhoea. If the patient is eating an ordinary hospital diet containing more than 50 g and less than 150 g of fat, usually about 70 to 80 g, the measurement of the average amount of fat in the stools collected for each 24-hour period for four consecutive days will give a satisfactory answer. The nitrogen and volatile fatty acids may be measured at the same time. If the figures obtained do not exceed those shown in Table I, steatorrhoea is not present. If these figures, especially that for long-chain fatty acids, are clearly exceeded, it is likely that the patient has steatorrhoea. In most of the patients under discussion here, the faecal fat level averaged 10 g a day or more. The daily analysis of faecal fatty acid may be carried on indefinitely. This method, originally described by van de Kamer *et al.*,[7] not only simplifies and speeds up the studies necessary for diagnosis, but also provides an excellent means of following the progress of the patient over a long period.

TABLE I

LIMITING 24-HOUR VALUES IN STOOLS

Long-chain fatty acids, g	5
Nitrogen, g	2
Short-chain volatile fatty acids, g ..	1

What is the fat in the stools? Where does it come from? It is hard to believe that such simple questions should be difficult to answer. It is a fact, however, that these questions cannot be answered satisfactorily in each individual patient at the present time. The reasons for the difficulty are certain peculiar features in the emptying of the large bowel, the existence of a number of possible sources of long-chain fatty acids in the stools and the inadequacy of many of the analytical methods available.

With regard to the nature of the fat: it has been known for many years that the fat in the stools is relatively more saturated than the dietary fats. This was originally shown by means of iodine values and melting-point determinations; such indices are far from satisfactory in the study of variable mixtures of fatty acids. Van de Kamer and Weijers[8] showed that the increased fatty acids in steatorrhoea tended to be saturated rather than unsaturated. The amount of saturated fatty acids put out sometimes exceeded the total amount of saturated fatty acids taken in. Recently, the faecal fats have been subjected to analysis by vapour-phase chromatography. Studies involving different types of chromatographic systems are necessary to arrive at a satisfactory final conclusion on fatty-acid composition. My colleagues, Sammons and Wiggs,[9] using these methods, have shown that there is a remarkably high stearic acid content in normal faecal fat. It accounts for some 40 per cent. of the total fatty acids present. This is interesting, because this level of stearic acid is not found in any other natural fat so far described. James, Webb and Kellock[10] have

shown that a number of oleic acid isomers and hydroxy-fatty acids, not present in the dietary fats, are found in stool fats, and they have also confirmed the high stearic acid content.

The origin of the long-chain fatty acids found in the stools may be from unabsorbed dietary fat, which may be unchanged or may be modified in some way during passage down the intestines. Alternatively, it may be derived from fats passed into the intestine from elsewhere, or from fatty acids synthesised in the intestinal lumen or wall from other substances. The high level of stearic acid might be due to selective and more effective absorption of other fatty acids. Relatively low digestibility of long-chain saturated fatty acids has been demonstrated[11] when large amounts are fed. This, however, is usually overcome by the presence of sufficient quantities of oils that are liquid at body temperature; these act as a vehicle for the higher-melting-point fats. The increase in stearic acid could also be due to hydrogenation of unsaturated C_{18} acids, such as oleic acid. The presence of oleic acid isomers and hydroxy-fatty acids not present in the diet also suggests modification of unabsorbed dietary fatty acids. The most likely modifying influence in the intestinal lumen is the intestinal flora. The flora are known to play a part in the modification of a number of substances in the stools—for example, the bile pigments. There are reasons for supposing that the intestinal flora are more active in conditions in which there is faulty absorption from the small intestine; this presumably reflects the improvement in food supplies. Bacterial activity may also account for the increase in volatile fatty acids and fluidity of the stools, and for the pale colour of the pigments in steatorrhoeic stools.[12] The question of bacterial synthesis of fatty acids from smaller fragments is of interest. There is no doubt that many micro-organisms can form fatty acids, but the fatty acid mainly produced is palmitic and not stearic acid. It seems probable that fatty acids formed by micro-organisms may contribute to the faecal fat level; there is no conclusive evidence at the present time that such a process can account for a major proportion of the stool fat.

Are there any other means of determining whether the faecal fat is directly derived from unabsorbed dietary long-chain fat? Clearly, labelled fats can be used. These may take the form of inactive or radioactive halogenated fats, or fatty acids labelled with isotopic carbon. None of these has proved entirely satisfactory. Halogenated fatty acids lose their original properties and may be treated as fully saturated fatty acids. A monochlor-mono-iodo-oleic acid derivative has some advantages over the di-iodo compound.[13] There is, however, always some doubt whether the iodine-131 label will remain firmly attached to the fatty acid, especially under conditions that might give rise to active hydrogenation. Fatty acids labelled with the stable carbon-13 isotope are of value, but in this country the supply of carbon-13 is restricted and the analytical procedures require specialised apparatus and experience. Carbon-14-labelled fatty acids may be used, but the range of fatty acids available has so far been limited. We have carried out a number of studies with fats doubly labelled with iodine-131 and carbon-14; in general, the two labels have shown close correlation. These studies have indicated that most of the patients under discussion to-day have a demonstrable defect of long-chain fatty acid absorption and that most of the increased faecal fat is directly derived from unabsorbed dietary fat. This does not, however, fully account for the increase of faecal fat in many of these patients. Similar results were obtained by Blomstrand,[14] using carbon-13-labelled fats. There are a few patients, however, especially a certain proportion of those with tropical sprue, who have a much greater amount of fat in the stools that does not appear, on present evidence, to be directly derived from unabsorbed dietary long-chain fat. In these patients, the increased faecal fat is dependent, in some way not yet understood, on the intestinal flora. The administration of effective doses of antibacterial agents causes a dramatic and permanent reduction in the faecal fat.[15] Similar material is without this striking curative effect in other patients with steatorrhoea.

It is possible that these labelled-fat studies may provide the final answer to this problem. As I have already indicated, it is important to bring the problem down to the molecular level; the type of labelled fatty acid used may be significant. Another complication is the incomplete emptying of the large intestine. Thus the unabsorbed residue of a single dose of labelled fat is spread over several days in the stools. A further problem arises from the use of radioactive-isotope labelled materials. It is generally agreed that it is desirable to keep radiation exposure to a minimum, especially in young people. Radiography is often needed in our patients and there are a number of other investigations in which the use of radioactive tracers may be necessary. It would be unwise, therefore, to confine development to methods involving the use of radioactive labelling; there is undoubtedly good scope for methods in

which stable isotopes are used. My colleagues, Sammons and Wiggs,[9] have recently developed a new technique that may prove to be of considerable value in this problem. They have interesterified erucic acid, a mono-ethenoid acid with a 22-carbon chain, into dietary fats and produced an acceptable food material containing significant amounts of erucic acid. If this unsaturated fatty acid is hydrogenated, it gives rise to behenic acid, which does not normally occur in the stools and can be readily identified and quantitatively determined by vapour-phase chromatography.

It is, I think, apparent that great advances have been made in the analysis of stool fats during the last few years, and it may be possible to answer the important questions about the nature and origin of faecal fats in each individual patient before long. It is also apparent how unsatisfactory some of the analytical methods have been; however, even with the development of more effective methods of chemical analysis, a full appreciation of all the biological factors involved is necessary before the results obtained can be usefully interpreted.

Let us now assume that the stool fats are markedly increased in the patient we are considering, to, say, an average daily level of 15 g, and that studies along the lines I have described have indicated that this extra fat was largely derived from unabsorbed dietary long-chain fat. We are immediately faced with the question—what is the cause of the defective absorption in this patient?

The factors concerned in fat absorption, which we now have to study, may be broadly divided into two groups: those that exert their effect in the intestinal lumen, where the fat is prepared for absorption, and those that are directly concerned with the uptake of the fatty material into the intestinal cells and its transport to blood vessels or lymphatics, which will convey it away from the intestine and make it available for the needs of the body as a whole. The intraluminar factors may be studied directly by intubation; the factors affecting the small intestine itself require the application of three groups of studies: measurement of the absorption rate of suitable index materials, radiographic investigations and biopsy.

We should perhaps spend a few moments considering these methods. Samples of upper small intestinal contents are easily withdrawn by intubation. The position of the tube should be checked radiographically. Over-all absorption studies can only be made with suitably labelled materials, as already described. Absorption-rate tests depend upon the administration of an index substance, with the subsequent serial estimation of the amounts of the substance present in the blood or the urine. The rate of accumulation or elimination is regarded as an index of the rate of absorption. This is, of course, true provided that the rate of removal from the blood or renal excretion remains constant during the experimental period. Perhaps the best known of such tests is the glucose-tolerance curve; in this case, however, it is well recognised that the increase in blood sugar stimulates insulin production and that the rate of removal of the glucose does not remain constant. We tried[16] to get round some of the difficulties a few years ago by administering the glucose by intraduodenal drip, which avoided difficulties due to delayed gastric emptying, and the complications of insulin release, by using a short experimental period of only 30 minutes. This method works well in adults. Another index substance used nowadays is the pentose sugar, xylose. This is metabolised less rapidly than glucose and appears in the urine; 20 to 25 per cent. of the dose administered should be recovered in 5 hours. There are many others, but I know of none that is without difficulties of interpretation.

A fat or fat-soluble index substance must also be studied. The chylomicrograph, labelled fat or vitamin-A-in-oil absorption curve may be used. They measure the rate of absorption of particulate fat.

Another group of absorption studies makes use of substances selectively absorbed in certain regions. One of the best examples is cyanocobalamin (vitamin B_{12}), which is only absorbed from the lower part of the small intestine. Its absorption can be studied by using radioactive-cobalt labelled material. This may give useful information on the functional integrity of the ileum. Further development of such regional absorption tests is likely in the future.

We were able to demonstrate[17] some years ago that the formation of large clumps often seen on radiographic examination of these patients was due to clumping of the opaque medium with excessive mucus secretion. A non-flocculable opaque medium reveals the true pattern of the intestine and permits studies on muscle tone and motility to be carried out.

Biopsy consists in the removal of a piece of small intestinal mucous membrane, and this can now be done by intubation. The structure of the mucosal specimen can be examined

by histological techniques or by electron microscopy. It can be subjected to analyses or investigated for enzyme activity. The potentialities of the method have not yet been fully realised.

The preparation of fat for absorption involves partial hydrolysis, which is brought about by pancreatic lipase, and fine emulsification, which is due to the combined action of bile salts and the main end-products of pancreatic lipolysis, lower glycerides and fatty acids.[18] The presence of adequate amounts of pancreatic lipase and bile salts can be readily determined in intubation samples withdrawn from the upper intestinal lumen. It is also possible to study the degree of fine emulsification of the fat that is achieved. I have often been surprised to find that direct examination of upper small intestinal contents, which, in my opinion, is an essential step in diagnosis, has been omitted. This is sometimes due to certain misconceptions, which have been, and may still be, widely held. The first is the view that hydrolysis of the faecal fat to a level of 80 per cent. or more excludes pancreatic enzyme deficiency. This is not correct. Hydrolysis of faecal fat can exceed 80 per cent. in a patient with no demonstrable pancreatic lipase. The differential analysis of faecal fat into neutral fat, fatty acid and soaps is rarely a useful procedure. Other studies on the stools thought to give information on pancreatic enzyme production may be equally irrelevant. A second fallacy is the belief that it is sufficient to measure only one enzyme, usually trypsin, and then conclude that all pancreatic enzymes are quantitatively similar to the one studied. Sheldon[19] has described a child with specific deficiency of pancreatic lipase and we have recently encountered a similar patient. Thirdly, many workers use substrates other than long-chain glycerides for the assessment of pancreatic lipase; there is no great difficulty in using the substrate that is specific for true lipases,[20] and this would seem to be preferable. Finally, before absence of pancreatic enzymes can be considered proved, a maximal stimulus to pancreatic secretion, usually secretin, should be administered. The small intestinal contents should also be examined for bile salts; a specific deficiency of bile salts occasionally occurs.[21] In the light of recent work,[22] the degree of conjugation of the bile salts might also be studied with advantage.

A certain number of the patients with steatorrhoea will be found to have defective pancreatic lipase or defective bile salts, giving rise to inadequate fine emulsification and consequent interference with fat absorption. If trypsin and amylase are deficient, there may also be defects in protein and carbohydrate absorption, giving rise to increased nitrogen loss and more extensive fermentative changes. These patients often have extremely voluminous stools, exceeding a litre a day, as compared with the normal volume of about 150 ml. Appropriate replacement commonly causes considerable improvement.

Sometimes the upper intestinal lumen contains large numbers of micro-organisms. In certain cases, such as infestation with giardia, a small flagellate organism, this may be the cause of the steatorrhoea and appropriate chemotherapy will effect a cure.[23] An increase in the bacterial population is not, however, necessarily associated with steatorrhoea and the significance of such changes remains obscure.

Proceeding with our study, we must now try to assess the functional integrity of the small intestine along the lines I have indicated. In many patients with pancreatic lipase deficiency, the small intestine will be found to be normal as judged by absorption-rate tests of water-soluble index substances, radiography and biopsy. If a fat or fat-soluble index substance is used, however, fat absorption will be found to be grossly deficient; as I have already mentioned, this is due to the faulty emulsification of the fat in the intestinal lumen.[24] In some of these pancreatic patients, however, the small intestine is not found to be functioning normally and this may easily lead to confusion. The abnormality of intestinal function in these patients is due to secondary water and electrolyte imbalance. This arises from the fact that these patients may lose 1000 to 1500 ml of fluid in the stools daily. This involves not only an extra loss of water, but a considerable loss of electrolytes. As the dehydrative process continues, potassium may be lost from the cells; this may be further encouraged by a progressive protein deficit. The depletion of water and electrolytes results in serious interference with cellular activity; the small intestine may become atonic, dilated and functionally ineffective.

How can one detect this complication? In recent years a great advance has been made in the estimation of electrolytes by the introduction of flame photometry. This permits rapid and repeated estimations of sodium and potassium to be carried out at frequent intervals, so that the water and electrolyte status of the patient can be kept under close review. Severe depletion of sodium, potassium and chloride is common in these patients. If the situation

is appreciated soon enough, it can be corrected by suitable replacement therapy. Rapid replacement is not without its dangers, but these can be minimised by careful therapeutic control. The effective treatment of water and electrolyte imbalance is life-saving. Here, indeed, is a triumph that improved methods of analysis have made possible. A further point about water and electrolyte studies may, however, be worth making. Examination of the levels in the blood is often valueless in the sort of patients we are considering; with developing dehydration, great variations in the volumes of the different water compartments in the body may occur, and the measurement of blood concentrations under such circumstances provides information that is often impossible to interpret. Provided that the kidneys are not seriously incapacitated, the examination of daily urine levels is much more informative. The kidney is the main regulatory organ for water and electrolytes; if depletion of a particular electrolyte occurs, the level in the urine falls markedly, and when repletion is achieved it soon returns to the more usual levels.

Other metallic ions may also be important. In patients with steatorrhoea this applies to calcium, iron and magnesium. Tetany due to lack of calcium or magnesium ions is not an uncommon complication. Knowledge of the rôle of magnesium is still fragmentary, but with the recent introduction of flame-photometric methods for both calcium and magnesium, there is every hope that much more information will be forthcoming in the near future.

All these secondary complications affecting the inorganic body constituents must be corrected under controlled conditions before more detailed study of the basic defect in the absorptive mechanism can be usefully carried out. Assuming that this has been done, we may now proceed to the study of the basic absorption defect in a patient in whom pancreatic lipase and bile salts have been found to be within the normal range. I should, perhaps, have mentioned earlier that intestinal changes, with consequent steatorrhoea, may occur as a complication of gastro-intestinal surgery or in association with other major pathological states, such as diabetes. Such problems are not under consideration here. Apart from these, the main changes affecting the small intestine and leading to steatorrhoea can be considered in four groups: those associated with lymphatic obstruction or disease affecting lymph glands, enteropathy due to intolerance to wheat gluten, tropical sprue and regional ileitis (Crohn's Disease). Although we have studied patients with each of these conditions, it will be sufficient for our purpose to examine one of them in detail.

The most suitable group of problems to put before you is concerned with patients with gluten-induced enteropathy. This condition accounts for almost all the children that were said to have coeliac disease and the adults diagnosed as suffering from idiopathic steatorrhoea or non-tropical sprue. The basic observation that these patients were intolerant to wheat gluten was made in children with coeliac disease by Dr. (now Professor) Dicke, of Amsterdam.[25] At the end of the war, during the acute bread famine in Holland, Dicke noticed that most of his patients were getting thinner day by day except for the coeliac children, who began to look better. Van de Kamer, Weijers and Dicke[26] in Holland, and our group[21,27] in Birmingham, were able to establish beyond any question of doubt that intolerance to wheat gluten was the basic cause of coeliac disease in children and idiopathic steatorrhoea in adults. This has since been widely confirmed in many parts of the world.[28,29] The withdrawal of wheat gluten from the diet results in striking improvement. Such a régime involves many changes, however, and we do not accept improvement on a gluten-free régime as a satisfactory criterion for the diagnosis of gluten-induced enteropathy. We insist on a definitive test consisting of the re-introduction of the gluten and the clear demonstration of an unequivocal increase of faecal fat to abnormal levels.[30] Such patients may be regarded as proved cases of gluten-induced enteropathy.

The first question I want to put forward is—what is the nature of the deleterious agent in wheat gluten? May I say immediately that it has nothing to do with the treatment of flour. Completely untreated flour, or gluten made from it, is just as effective in causing deterioration in these patients as flour treated or over-treated with chlorine dioxide or other oxidising agents. We have made an extensive study of the effect of chlorine dioxide on wheat flour, in another connection, and can find no evidence for any harmful or undesirable effects resulting from this treatment.

The deleterious effect in patients with gluten-induced enteropathy is confined to wheat and rye; other cereals and food proteins appear to be harmless. Acid hydrolysis or deamidation with acid or papain destroys the deleterious agent; however, peptic - tryptic

digestion leaves it unaffected; the peptic - tryptic hydrolysate can be autoclaved and ultrafiltered without loss of activity. Further incubation of this fraction with small-intestinal mucous-membrane extract renders it innocuous. It would seem, therefore, that the deleterious agent is a relatively small, heat-stable, molecule present in the gluten fraction.

The second question is—what effect does it have on the intestine? The two main changes observed are mucosal damage and alteration in the tone and motility of the intestinal musculature. Most workers in the field have reported poor recovery of mucosal damage even in patients showing a good clinical and biochemical response. Some have,[31] in fact, concluded that the mucosal changes are irreversible. I do not agree with this view, since we have clearly demonstrated reversibility of the mucosal damage in some patients. I have little doubt that reversibility will be more generally observed when we have a better understanding of all the factors involved. We would agree, however, with the general opinion that the mucosal changes may recover slowly and are not always well correlated with the clinical state of the patient. It may be that the motility changes are more important. They do recover more rapidly and have been shown to return early when gluten is re-introduced into the diet after a period of remission.[21]

The effect of the deleterious agent has been thought by some to be an allergic phenomenon.[32] However, there is little supporting evidence; the effect on the intestine is opposite to that commonly observed in allergic states; there is no indication of the frequent occurrence of other allergic manifestations in these patients. It can be shown that the effect in gluten-induced enteropathy is not due to any of the soluble antigens present in wheat gluten. Allergic phenomena that have been observed from time to time might be secondary to intestinal damage.

The other possible mechanism is a more direct action. In this connection recent studies with my colleagues, Schneider, Bishop and Shaw,[33] are of considerable interest. The fraction obtained after peptic - tryptic digestion, autoclaving and ultrafiltration causes inhibition of motility in the isolated rat's intestine. This effect is not obtained if the material is introduced into the lumen of the intestine, but can be readily demonstrated if it is applied to the outside. Incubation with mucosal-membrane extract destroys the activity enzymatically. Pharmacological analysis of the effect shows that the inhibition is due to interference with acetylcholine release. These observations have not been finally tied up with the clinical studies; this is being done at the present time. It seems highly probable that this is the mechanism of action of gluten in these patients. If this can be established, it will greatly facilitate further chemical analysis of the deleterious agent.

My last question is—why is wheat gluten not tolerated by these particular patients? Normal people can take 30 g or more of wheat gluten daily without any noticeable effect; the patient with gluten-induced enteropathy is made seriously ill by an intake of 10 g a day or much less. The deleterious agent in the gluten does not seem to be affected by peptic - tryptic digestion, but it is rendered innocuous by digestion with mucous-membrane extract. This is a heat-labile effect, which is presumably enzymatic. This has been shown in patients with gluten-induced enteropathy, as well as in studies on isolated intestinal preparations. The normal person has enzymes in the intestinal mucosa that render the deleterious agent harmless and it seems likely that these are deficient in the mucosa of the patient with gluten-induced enteropathy. Direct proof of this has not yet been obtained.

Some evidence of faulty handling of gliadin has been put forward by van de Kamer and Weijers.[34] They have shown that there is a greater rise in the blood glutamine after gliadin feeding in a patient with coeliac disease than occurs in a normal subject. This has been confirmed by others. The glutamine in the blood is not free, but bound, and the rise may be indicative of faulty breakdown of glutamine-containing derivatives. We and others have observed peptides in the blood of patients with gluten-induced enteropathy from time to time.[35] Unfortunately, the reliability and specificity of the increased blood-glutamine curve as a diagnostic test for gluten-induced enteropathy have been questioned.[36] Further work on this method is urgently needed.

That loss of protein can occur from the intestinal tract has been recognised for some time and is usually detected by the presence of increased nitrogen in the stools. It is obvious, however, that the nitrogen loss in the stools might also be due to excessive mucus secretion, or to faulty protein absorption. Increased nitrogen loss is commonly observed in patients with steatorrhoea, being more severe in patients with pancreatic trypsin deficiency. It has only recently been appreciated that considerable loss of protein may occur into the intestine

without any significant increase of nitrogen in the stools. This protein loss may be sufficient to cause severe hypoproteinaemia and consequent oedema. The explanation of this situation is that the protein leaks out into the upper small intestine, is digested and re-absorbed. The amino acids are re-utilised. If the leakage is rapid enough, the rate of loss of plasma proteins may be greater than the rate of replacement; if this is so, hypoproteinaemia must occur. The extent of the loss into the intestinal lumen can be measured by injecting iodine-131-labelled polyvinylpyrrolidone (PVP), which is a molecule about the same size as albumin. The PVP leaks into the intestinal lumen, but is not digested or absorbed, and so passes into the stools.[37] A normal individual passes less than 1·0 per cent. in the stools; usually about 0·1 per cent. In a patient with a protein-losing enteropathy, who has been under our care recently, 26 per cent. of the administered PVP was recovered from the stools. Biopsy in this patient revealed dilated lacteal vessels and intestinal lymphatics. Gordon[38] has made similar observations in his patients with protein-losing enteropathy. Whether lymphatic obstruction is a feature of all the patients in this group remains to be seen. These studies, again, reveal the importance of using different methods that cross-check to ensure correct interpretation.

So much for the problems that I wanted to put before you. I hope they have clearly illustrated the vital part played by chemical analysis at every step—differential diagnosis, therapeutic control and the investigation of pathogenesis. What are the special points of importance in the application of chemical analysis to the study of medical problems? I would put first the value of easier and more speedy methods of analysis. Cumbersome, time-consuming methods have done much to prevent the effective use of chemical analytical data in medical problems. With a deteriorating patient, one cannot afford to wait long for results. Serial studies may be virtually impossible with slow and elaborate methods. Excellent examples of the effect of such improvements can be seen in the studies using the daily-fatty-acid method for faecal fats and the control of water and electrolyte problems. Secondly, the importance of more precise methods, which permit problems to be studied at the molecular level. This is well illustrated by the application of vapour-phase chromatography to the problem of the nature and origin of the faecal fat and to the use of isotope-labelled or identifiable substances. Thirdly, it seems wise to make direct rather than indirect investigations when this is possible, as exemplified by direct assessment of pancreatic lipase activity in upper intestinal contents.

Fourthly, the need for close integration between the biologists and the chemists concerned in such studies is apparent at almost every step. The choice of the appropriate study in the patient and the safeguarding of the patient's welfare must obviously be in the hands of the doctor, the interpretation of absorption-rate tests, electrolyte concentration or faecal-nitrogen levels demand a full appreciation of the biological factors involved, and the development of better methods of analysis and sometimes their interpretation may require the attention of experienced chemists. In each problem, however, the chemical aspects, the biological factors and the medical problems must be weighed up together; none can exist in isolation; team-work is essential to progress in this field.

Fifthly, links with other related fields are needed. This can be seen in the studies involving food research and the preparation of gluten fractions in connection with the microbiological problems of intestinal flora and the pharmacological analysis of the action of gluten. Such help is often needed to bring a part of the problem to the point where chemical analysis can be usefully applied; this is certainly the case with the studies on the deleterious agent in gluten. Detailed analysis and identification could not be usefully done on the quantities of material needed for testing the fractions in patients, a daily dosage of 10 g of gluten being the standard used; with an isolated-tissue assay system responding to milligram or microgram quantities, fractionation, analysis and identification are greatly simplified.

In conclusion, may I be allowed to make one of those broad generalisations which some regard as one of the privileges of the nineteenth century and Bernard Dyer's generation. If the full impact of the latest developments in chemical analysis is to be effectively used for the advancement of medical knowledge and the care of the sick, we shall need many more recruits drawn from both the chemical and biological fields. The chemists must acquire sufficient understanding of the biological issues involved, and the biologists, amongst whom I include doctors, must know enough chemistry, so that these two groups can work in close association. There are, of course, such combined groups at the present time, but they are altogether too few in number. I do not believe that this dual requirement for the effective

application of chemical analysis to ensure medical progress is fully appreciated in all the places that it should be. There are certainly few opportunities at the present time for chemistry graduates to acquire the necessary biological or medical knowledge they need; I am not satisfied that this is adequately covered simply by allowing people to work for a higher degree in a biological atmosphere—some level of formal training is, I believe, necessary. The opportunities for medical or biological graduates to learn more chemistry are even fewer. Many medical students are quite inadequately trained in chemistry and this imposes further limitations on their education in biochemistry and related subjects. In my view, the contribution made so far by chemical analysis to medical progress is only a small fraction of its true potential. There is an urgent need for radical reorganisation of the education of medical students in chemistry and biochemistry; more opportunities must be provided for chemists, biologists and medical graduates to pursue appropriate graduate studies that are planned to ensure closer integration. If this lecture has done anything, however small, to draw attention to these needs, it would, I believe, have had the approval of Bernard Dyer.

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The Determination of Chemical Antioxidants in Fats after Separation by Partition Chromatography*

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Reverse-phase partition chromatography is used to separate butylated hydroxyanisole and the gallate esters from fat. The gallate esters are determined colorimetrically after reaction with ferrous tartrate, and butylated hydroxyanisole after reaction with 2:6-dichloroquinone chloroimide.

A method is described for determining butylated hydroxytoluene in ethanolic solution; it depends on measuring the ultra-violet absorption spectra of strongly alkaline solutions of butylated hydroxytoluene. The method is specific for butylated hydroxytoluene among the permitted antioxidants, but has not yet been successfully applied to its determination in fats.

The quantitative determination of antioxidants in fat involves in the first place their separation from the fat. Methods of separation described in the literature include extraction,[1,2] steam-distillation at elevated temperature[3] and chromatography on moist silica.[4] The application of reverse-phase partition chromatography is described here for this purpose, Silastic 181 (a synthetic rubber) being used as the inert support. The possibility of using both natural and synthetic rubbers for partition chromatography was first suggested by Boldingh.[5] Light petroleum (boiling range 40° to 60° C) is used as the stationary phase and 60 per cent. acetone as the mobile phase. It has not been possible to separate the antioxidants from each other by this technique, but specific methods for determining the gallates and butylated hydroxyanisole (BHA) in the eluate are available.

It was found that the method proposed by Vos, Wessels and Six[2] was suitable for determining the gallates in the aqueous acetone eluates after minor modifications to adapt the procedure to our conditions; it involves reaction with ferrous tartrate and then extraction of the reaction mixture with *iso*amyl alcohol. The purple colour given by octyl or dodecyl gallate is measured in the *iso*amyl alcohol solution, and that derived from propyl gallate can be measured in the aqueous phase.

The determination of BHA has been effected after reaction with 2:6-dichloroquinone chloroimide, a method first introduced by Mahon and Chapman.[1] At first, considerable variations in the colour given by known amounts of BHA were observed. Further, the presence in the test solution of some gallate ester (as might occur in the analysis of commercial fats) caused an increase in the intensity of the colour obtained, although gallates themselves do not react. Investigation of the variables involved showed that the temperature of reaction had a marked effect on the intensity of colour finally reached; more intense colours were obtained at lower reaction temperatures, with an optimum at about 0° C. Optimum values for the pH of the buffer and the solvent composition of the reaction mixture have also been established. When the conditions giving maximum colour development are used for the reaction, no interference is caused by the presence of gallate esters.

A specific method for determining butylated hydroxytoluene (BHT) in ethanolic solution has been devised; it is based on measuring the ultra-violet spectrum of the ionised form of BHT in strongly alkaline solution. Ionisation causes a shift in the absorption maximum from 278 to 306 mμ,[6] and, although this behaviour is characteristic of many phenols (including BHA), it has been found that the alkaline solution of BHT is relatively unstable. The decrease in absorption at the peak wavelength (306 mμ) after storing the solution under controlled conditions gives a quantitative measure of the BHT present. Under the same conditions the ionised form of BHA is relatively stable, and only a small change in absorption at 306 mμ occurs; a correction would need to be applied in analyses of mixtures of BHT and BHA. The ultra-violet spectra of the gallates in alkaline solution have been shown to have no characteristic absorption band. The small absorption at 306 mμ does not change appreciably on storage of the solution, and the presence of gallates should therefore not interfere with this method of determining BHT.

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The method was devised for determining BHT in the chromatographic eluates from fats, but accurate quantitative results have not yet been obtained in this application. The matter is being investigated, and it is hoped that a further communication on the subject will be made in due course.

METHODS

Preparation of Silastic 181—

Advice on the supply of Silastic 181 can be obtained from Midland Silicones Ltd.

Cut the Silastic into small pieces, and pass them through a hammer mill once with a coarse or medium sieve and then a second time with a fine sieve. Pass the powdered Silastic through a sieve, retaining the fraction between 50 and 150 mesh. This is most conveniently done by immersing the sieve in acetone and brushing the powder through with a clean paint brush. Allow the solvent to evaporate. Heat the sifted powder to boiling with 5 *N* hydrochloric acid, stir well, decant, and repeat this operation until the washings are free from iron. Wash the powder repeatedly with hot distilled water until the washings are free from chloride, and then extract the powder repeatedly with hot acetone until only a negligible amount of material is removed.

Preparation of columns and separation of antioxidants—

Use analytical-reagent grade light petroleum (boiling range 40° to 60° C) as the stationary phase and 60 per cent. acetone (300 ml of redistilled acetone *plus* 200 ml of water) as the mobile phase. Shake the solvents together, and then de-oxygenate by passing oxygen-free nitrogen through them; use these mutually saturated solvents throughout.

Add 5 ml of light petroleum to 5 g of Silastic, and stir until absorbed. Make into a slurry with 60 per cent. acetone, and transfer the slurry to a chromatographic tube. Run off excess of mobile solvent until the Silastic just remains covered. It has been found convenient to use a tube about 35 cm long, the upper 20 to 25 cm being wider (2·5 cm diameter) than the lower portion (1 cm diameter). The tube is water-jacketed and maintained at 21° C.

Weigh 3 to 4 g of fat, and dissolve it in the minimum amount of light petroleum. Add 1 g of dry Silastic for each gram of fat and each millilitre of solvent used. Stir well, make into a slurry with the mobile solvent, and transfer to the column. Use 2 to 3 ml of light petroleum to rinse the beaker, and absorb in 3 g of Silastic. Transfer this to the column with 60 per cent. acetone.

Wash the column with 60 per cent. acetone at the rate of about 150 ml per hour. Collect 200 ml *plus* 100 ml of eluate, and analyse separate portions of these eluates for BHA and for gallate esters. When the sample contains not more than about 300 μg of these antioxidants they will normally be present in the first 200 ml of eluate, and the collection of two separate fractions avoids the unnecessary dilution that would result from collecting one 300-ml fraction.

Determination of butylated hydroxyanisole

Reagents—

Ethanol, 95 per cent.—Analytical-reagent grade.

2:6-Dichloroquinone chloroimide reagent solution—A 0·02 per cent. solution of 2:6-dichloro-*p*-benzoquinone-4-chloroimine in 95 per cent. ethanol.

Buffer solution, pH 9·8—Mix two volumes of 0·05 *M* sodium carbonate with one volume of 0·05 *M* sodium tetraborate, both solutions having been prepared from analytical-reagent grade salts.

Procedure—

Take 10-ml aliquots from each fraction in 25-ml calibrated flasks. Add 6 ml of 95 per cent. ethanol to each, and cool to 0° C. Add 2 ml of 2:6-dichloroquinone chloroimide reagent solution previously cooled to 0° C. Mix, and add 3 ml of buffer solution previously cooled to 0° C. Mix, and allow the colour to develop for 1 hour at 0° C; then set the solution aside (for about 30 minutes) until it has reached room temperature, and make up to the mark with 60 per cent. acetone.

Measure the optical density against 60 per cent. acetone in 4-cm cells at 610 mμ with a Unicam SP600 spectrophotometer. Calculate the BHA content of the fractions by using a standard graph prepared by measuring under the same conditions the optical densities of known amounts of BHA (up to 40 μg).

Determination of gallates

Reagents—

Ferrous tartrate reagent solution—Dissolve 0·1 g of ferrous sulphate and 0·5 g of Rochelle salt in 100 ml of distilled water. Before use, add to 10 ml of this solution 2 ml of a 2 per cent. solution of sulphur dioxide in water, and set aside for 10 minutes.

Sodium acetate solution—A 1 per cent. solution of sodium acetate (analytical-reagent grade) in water.

Amyl alcohol—"*iso*Amyl Alcohol for Milk Testing."

Extraction solvent—Equal volumes of amyl alcohol and light petroleum (boiling range 40° to 60° C).

Acetone—Redistilled.

Buffer solution, pH 4·6—Mix four volumes of 0·1 *M* potassium hydrogen phthalate with one volume of 0·1 *M* sodium hydroxide, both solutions having been prepared from analytical-reagent grade salts.

Procedure—

Measure 60 to 80 ml of eluate into a 250-ml separating funnel. Add 1·2 ml of the freshly "reduced" ferrous tartrate reagent solution. Add a volume of sodium acetate solution equal to the volume of eluate taken. After 10 minutes extract the solution first with 20 ml and then with 15 ml of the extraction solvent. Dilute the combined extracts to 50 ml with amyl alcohol, and determine the higher gallates by measuring the optical density in a 4-cm cell at 532 mμ with a Unicam SP600 spectrophotometer.

Determine propyl gallate by measuring the optical density of the aqueous phase at 532 mμ after diluting to 200 ml with acetone. (In view of the weak colours obtained, we have preferred to make this measurement in a 20-cm cell on a Spekker absorptiometer with a Chance OG1 filter.)

Calculate the gallate content of the solution by the use of standard graphs prepared by treating known amounts of each of the gallate esters (up to a total of 200 μg) by the method described above.

A qualitative test for differentiating between octyl and lauryl gallates has been described by Vos, Wessels and Six,[2] but it was found to be useless when applied to the eluates obtained by the chromatographic method.

The test described below has, however, been shown to distinguish between the two higher gallates.

Carry out the ferrous tartrate reaction on about 20 ml of the eluate, as described above, but use the phthalate buffer solution in place of the sodium acetate solution, and extract with 5 ml of the extraction solvent. A blue colour is given in the upper layer by lauryl gallate, whereas no colour is obtained in either layer with octyl gallate. It is hoped that this test may be developed into a quantitative method specific for lauryl gallate; however, for many purposes a qualitative differentiation between the two gallates is all that is necessary.

Determination of butylated hydroxytoluene

Reagents—

Ethanol, 80 per cent.—Dilute 80 ml of ethanol (analytical-reagent grade, 99 to 100 per cent., optical transmission at least 95 per cent. at 270 mμ) with 20 ml of water distilled in all-glass apparatus. De-oxygenate before use by bubbling oxygen-free nitrogen through the solvent.

Potassium hydroxide solution—Place 47 ml of water distilled in all-glass apparatus in a 200-ml flask. Pass a slow stream of oxygen-free nitrogen through the water for about 10 minutes. Add 53 g of analytical-reagent grade potassium hydroxide, and continue the passage of nitrogen until complete solution is effected. Insert the stopper in the flask, and set aside until cool. This alkali may be prepared in larger quantities and stored, preferably in a polythene container.

Procedure—

Measure 10 ml of BHT solution in 80 per cent. ethanol (containing 10 to 100 μg of BHT) into a 15-ml glass-stoppered calibrated flask, and cool to between 0° and 5° C. Add by pipette (preferably of the syringe type) 4 ml of potassium hydroxide solution, mixing well during addition to prevent formation of a separate layer of alkali. Dilute to the mark with 80 per

cent. ethanol. Exactly 5 minutes after beginning to add the alkali, measure the optical density at 306 mμ in a 4-cm cell against distilled water. Return the solution to the flask, and place the flask in a thermostatically controlled bath at 31° C. After holding for 2 hours at 31° C again measure the optical density at 306 mμ.

Treat 10 ml of pure solvent by the procedure described above. Only a small increase in the optical density of the blank solution (less than 0·010) should occur after holding at 31° C. Subtract the corresponding readings from those obtained for the BHT solution to give the net optical densities.

The alkalinity of the final solution should be checked by titration and ought not to lie outside the limits 3·0 to 3·2 *N*.

The decrease in the net optical density after holding at 31° C has been shown to be a measure of the concentration of BHT, a drop of 0·33 being obtained when 100 μg of the antioxidant are present in the 10 ml of solution taken for the determination.

TABLE I

RECOVERY OF MIXTURES OF ANTIOXIDANTS

	Butylated hydroxyanisole			Octyl gallate			Propyl gallate		
	Added, μg per g	Found, μg per g	Error, μg per g	Added, μg per g	Found, μg per g	Error, μg per g	Added, μg per g	Found, μg per g	Error, μg per g
Groundnut oil ..	—	—	—	39	43	+4	64	60	−4
	—	—	—	66	77	+11	38	40	+2
Palm-kernel oil..	189	193	+4	42	38	−4	—	—	—
	134	133	−1	10	11	+1	—	—	—
	97	96	−1	99	103	+4	—	—	—
	95	98	+3	45	50	+5	—	—	—
	199	199	0	—	—	—	61	64	+3
	202	209	+7	—	—	—	101	101	0

RESULTS AND DISCUSSION OF THE METHOD

The results obtained for analyses in which known amounts of BHA or of one of the gallate esters were added to fats are shown in Fig. 1. The fats used were palm-kernel oil, groundnut

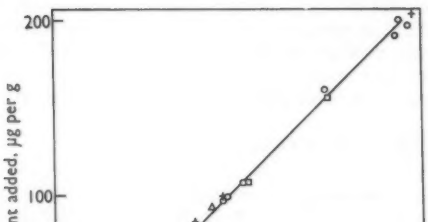

Fig. 1. Recovery of antioxidants added to fats: ○, butylated hydroxyanisole; □, propyl gallate; +, octyl gallate; △, lauryl gallate

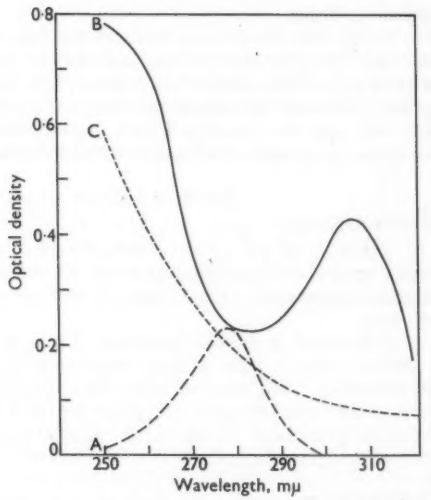

Fig. 2. Ultra-violet absorption spectra of butylated hydroxytoluene: curve A, in 80 per cent ethanol; curve B, 5 minutes after addition of alkali; curve C, after standing for 2 hours at 31° C

oil and suet fat, and in addition to these results the method has been applied successfully to the determination of octyl gallate in orange oil (995 μg per g added; 980 μg per g recovered). Results obtained for analyses in which a mixture of two permitted antioxidants has been added to fats are shown in Table I. A satisfactory degree of accuracy has been attained in all these determinations.

The ultra-violet spectra for BHT, BHA and octyl gallate (100 μg in 15 ml of solvent) are shown in Figs. 2, 3 and 4, together with the corresponding spectra after the addition of alkali and after storing the alkaline solutions at 31° C. For the treatment with alkali, 100 μg of antioxidant were also taken, and the procedure described for the determination of BHT was followed in each instance.

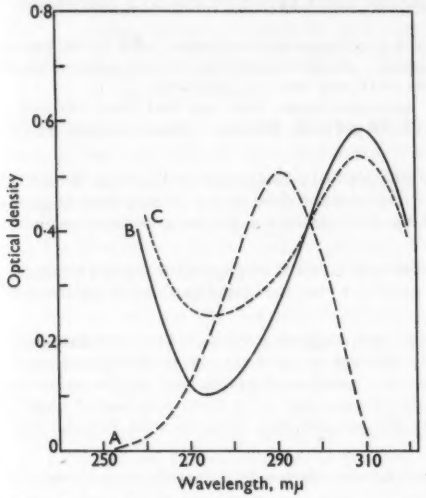

Fig. 3. Ultra-violet absorption spectra of butylated hydroxyanisole: curve A, in 80 per cent. ethanol; curve B, 5 minutes after addition of alkali; curve C, after standing for 2 hours at 31° C

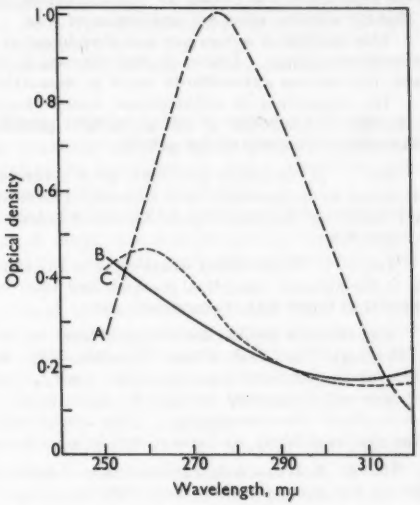

Fig. 4. Ultra-violet absorption spectra of octyl gallate; curve A, in 80 per cent. ethanol; curve B 5 minutes after addition of alkali; curve C, after standing for 2 hours at 31° C

The procedure adopted is empirical, and a similar effect can be obtained by setting aside at lower temperatures for a longer time. The conditions described are conveniently available in our laboratory, and it is not suggested that an alternative standardised method could not be devised.

It can be seen from Figs. 2 and 3 that the absorption maximum at 306 mμ for BHT disappears completely after storage for 2 hours at 31° C, whereas only a small change occurs in the absorption spectrum of BHA (maximum at 309 mμ) under the same conditions. The change in the net optical density of the alkaline solution of BHA at 306 mμ is about 14 per cent. of that exhibited by a solution of BHT at the same concentration, and a correction (calculated from the pre-determined amount of BHA present) will be necessary if it is eventually possible to apply these observations to the determination of BHT in fats.

We thank Dr. E. B. Hughes for his interest and encouragement and the Directors of J. Lyons & Co. Ltd. for permission to publish.

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Discussion

Mr. J. Markland congratulated the authors on their interesting paper and said that he was sure that he could speak for Public Analysts and say that they were indebted to the Food Industry for contributing valuable material on a problem common to local authorities and manufacturers.

He had been working on this problem and had used a similar method of partition chromatography, but different materials. This work started with the qualitative detection of antioxidants by reverse-phase chromatography on paper impregnated with liquid paraffin (Markland, J., *A.P.A. Bulletin*). This was followed by attempts at separation on a silica column with dilute alcohol as the stationary phase and light petroleum as mobile phase. The gallates were completely removed, but butylated hydroxyanisole passed through. This confirmed the authors' experience. However, if traces of iron were removed from the silica by washing with hydrochloric acid or if an acidified alcohol was used as the stationary phase, some separation was obtained. The retention of the gallates might have been due to a combination of a slightly alkaline silica gel and traces of iron.

This method of separation was abandoned in favour of polythene columns treated with liquid paraffin as stationary phase. Dilute alcohol was used as mobile phase. By increasing the concentration of alcohol used, the various antioxidants could be separated. This work was not yet completed.

The separation of antioxidants, except butylated hydroxytoluene, from fat had been effected by extraction of a solution of the fat in light petroleum with 80 per cent. alcohol. Three extractions gave quantitative recovery of the gallates.

Mr. C. B. Stuffins said that, after a considerable amount of investigation, it had been found that butylated hydroxytoluene was certainly the most difficult to extract from fats. It had been suggested that butylated hydroxytoluene formed a complex with the fat, and this might be a possible reason for the difficulty.

Dr. E. C. Wood asked where Silastic 181 could be obtained; could it be purchased ready prepared for use in the authors' analytical method, and what led the authors to try this substance out of all the many others that might have been considered.

Mr. Berger replied that Silastic was one of the materials suggested for partition chromatography by Boldingh (*Rec. Trav. Chim. Pays-Bas*, 1950, **69**, 247), although he gave no actual example of its use. Mealorub (a powdered natural rubber used by Boldingh) was found to discolour and oxidise somewhat, and was not considered suitable for their work. Silicone rubbers were very inert and almost ideal for reverse-phase chromatography. After consultation with Midland Silicones they selected Silastic 181 as being the least likely to contain interfering substances.

Mr. K. A. Hyde asked if the study of antioxidants in fats in relation to induction period threw any light on the potential life of antioxidants in fats.

Mr. Berger said that the work described had not dealt with the effectiveness or mode of action of the antioxidants, but it was considered that their methods would be useful in investigating these problems.

Mr. H. S. Young enquired if it could be assumed that no oxidation of the fat would take place so long as there was even a trace of antioxidant present.

Mr. Berger replied that this was a matter that had been extensively investigated (J. H. Mahon and R. A. Chapman, *J. Amer. Oil Chem. Soc.*, 1953, **30**, 34 and 1954, **31**, 108), and it appeared that oxidative rancidity occurred before the antioxidant was completely destroyed.

Mr. G. S. Ingram said that the authors stated that a reaction period of one hour was allowed for the reaction between butylated hydroxyanisole and Gibbs' reagent. Was this quite necessary for both alcohol and acetone.

Mr. Berger said that the conditions specified for the Gibbs' reaction were found to give maximum colour development when butylated hydroxyanisole was dissolved in the eluting solvent used in their chromatographic separation. It was quite possible that other optimum conditions would obtain when a different solvent was used.

Dr. W. E. Elstow said he had found that, in aqueous solutions at least, the rate of colour development from butylated hydroxyanisole and Gibbs' reagent depended on the pH and that, although some time had to be allowed for the colour to develop at pH 9·3, the development reached the same maximum almost immediately at pH 10·4.

Dr. J. H. Hamence asked whether any attempts had been made to separate the individual antioxidants by paper chromatography after column separation. From his experience in this matter it seemed to him that the various antioxidants were substances that should lend themselves to separation by paper chromatography.

Mr. Berger replied that they had aimed at an accurate determination of permitted antioxidants and that they had not made any attempt to analyse their eluates by paper chromatography. Complete separation of the antioxidants by paper chromatography had not yet been effected, but it would provide a useful method of identification in due course.

The Determination of Beryllium Metal in Air*

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Methods are described for the sampling and testing of air in a laboratory designed and equipped for work on beryllium metal.

A suitable volume of air is drawn through a filter-paper. The paper is destroyed by wet oxidation, and any beryllium present is collected by co-precipitation, redissolved and determined on a direct-reading spectrograph.

The method has been shown to be satisfactory over the range 0·015 to 50 μg of beryllium. The total time required for testing twenty samples is about 4½ hours.

THERE is an intense interest in the metal beryllium, arising from its potential value as a canning material for the fuel elements of nuclear reactors. Because of the extremely toxic nature of this element special precautions are taken in handling it, even when the small quantities required for experimental and development work are involved.

The most important danger to be feared is the inhalation of the metal or of its compounds in a finely divided form, and to prevent this a most elaborate ventilation system has to be installed for protecting not only those working with the metal, but also others both inside and outside the building.

All air leaving the beryllium laboratory is passed through filters guaranteed to remove 99·95 per cent. of particles in the range 0·1 to 0·5 μ diameter; larger particles are removed even more efficiently. The air in various parts of the building is changed from 10 to 30 times per hour, fresh air being blown in, also through filters, to replace that extracted. The quantity of air extracted is, however, greater than that admitted, so that a slight negative pressure exists inside the building and leakage can occur only inwards.

In addition to these general provisions, all operations that can lead to the formation of beryllium dust or chippings are performed inside working boxes or hoods, which are separately ventilated, with an inlet air velocity of from 200 to 500 feet per minute across the working face.

To check the effectiveness of the ventilation scheme, methods for determining sub-microgram amounts of beryllium are required. The three "maximum permissible levels" generally accepted in the United States and in this country are—

(1) The atmospheric concentration of beryllium in a laboratory should never be greater than 2 μg per cubic metre averaged over an 8-hour working day.

(2) In no circumstances and at no time should the concentration of beryllium in the air exceed 25 μg per cubic metre, even though the daily average might be satisfactory.

(3) The concentration of beryllium in the air in the vicinity of a plant handling beryllium should never exceed a monthly average of 0·01 μg per cubic metre.

A continuous-monitoring technique would in principle be ideal, but when this work was begun no commercial equipment for the purpose had been in use long enough to confirm its reliability. A batch-sampling method has therefore been evolved. Air samples taken at the beryllium laboratory of the G.E.C. Atomic Energy Division at Erith are divided into three categories—

(1) Environmental samples, to ensure the safety of those outside the building, are taken daily from the exhaust stack of the ventilation system on the exit side of the filters.

(2) Background samples are taken in the laboratory at a distance of at least 5 feet from any operation involving the handling of beryllium; this is to ensure that the main body of air in the room is safe for those not protected by special breathing equipment.

* Presented at the meeting of the Society on Wednesday, October 7th, 1959.

(3) Specific samples are taken in the immediate vicinity of operations in which beryllium is processed or handled. Routine operations are frequently checked by two or three sampling instruments in this way. Any new operation is checked by a larger number of samples taken on every occasion, and, until the results consistently show that the process does not involve the dispersion of beryllium dust, the operator wears fully protective clothing and has an external air line for breathing.

Swab samples are also taken, with moist filter-paper, both from exposed surfaces in the laboratory and from any equipment that it is proposed to remove from the building. These are analysed in the same way as the air samples.

The method of analysis used resembles that of earlier workers (*e.g.*, Cholak and Hubbard[1]) in that the filter-paper is submitted to wet oxidation, the beryllium is co-precipitated with calcium phosphate and the redissolved beryllium is finally determined spectrographically. The procedure has, however, been considerably shortened and simplified; the main differences from the earlier method being—

(1) The wet oxidation is made more rapid by the addition of bromine to the nitric - sulphuric acid mixture.

(2) The "spectroscopic buffer solution" containing chlorides and phosphates of sodium, potassium, calcium and magnesium is omitted.

(3) Gold is used as internal standard instead of thallium, and this is added together with the hydrochloric acid used to dissolve the calcium phosphate.

(4) The porous-cup method[2] with condensed-spark excitation is used instead of the arc method.

(5) A direct-reading spectrograph is normally used, photographic measurement being occasionally employed for reference purposes.

The method described has been used only for samples consisting of beryllium metal and such oxide as is produced by atmospheric oxidation. Modification of the chemical treatment might well be required to deal with beryllia refractories or other beryllium compounds.

Experimental

Collection of samples—

The air-sampling instruments used for "specific" and "background" samples are small pumps (Vacandair*) drawing approximately 10 litres of air per minute through a hardened filter-paper (Whatman No. 541). "Environmental" samples are taken with an Electrolux - Fleming Radio sampler† of about ten times this capacity.

Little information is available on the efficiency with which conventional filter-papers retain fine particles carried by a stream of air. The probability of loss of the finest particles increases as the air velocity through the paper increases, and this conflicts with the desirability of taking a large volume of air when determining contamination at such extremely low levels. More efficient filters either require much higher pressures to force air through them (*e.g.*, membrane filters) or they introduce difficulties into the wet-ashing procedure (*e.g.*, glass-fibre papers).

Fortunately, several factors operate to make the sampling procedure more efficient in practice than might be expected from the calculations made by Hounam and Wilkins.[3] They also mention that the efficiency of a filter increases over the period of use, as the larger pores become blocked by dust particles. Also, extremely small particles diffuse rapidly and thus collide with and adhere to other particles before they have been dispersed for very long. Finally, there is some evidence[4] to suggest that 80 per cent. of particles 0·2 to 0·3 μ in diameter are not retained by the lungs, but are exhaled, so that these finest particles, which may escape a filter-paper, are of much less importance than the larger ones.

The filter-paper circles used for both types of samples are 5·5 cm in diameter. For transport to the analytical laboratory it was considered that enclosing the sample paper,

* Obtainable from Aerosol Products (Colchester) Ltd., 87, Eccleston Square, London, S.W.1.
† Obtainable from Fleming Radio (Developments) Ltd., Caxton Way, Stevenage, Herts.

even if folded, in an envelope from which it was later to be removed for analysis might lead to loss of beryllium. Each filter-paper is therefore transferred with forceps from the sampler head into a transparent cellophane envelope, which fits it without folding, and on reaching the analytical laboratory the envelope is treated with the paper still inside it.

CHEMICAL TREATMENT—

Both the sulphuric acid and the bromine - nitric acid mixture are added from vacuum-operated constant-volume dispensers (see Fig. 1) for speed and safety. To operate, the glass

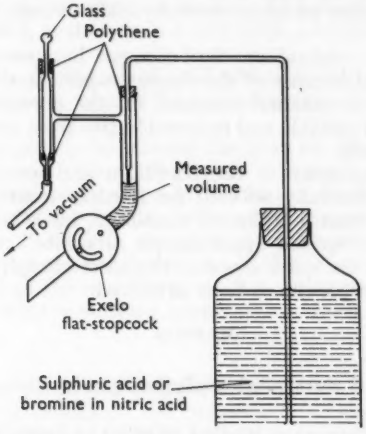

Fig. 1. Dispenser for sulphuric acid or bromine in nitric acid

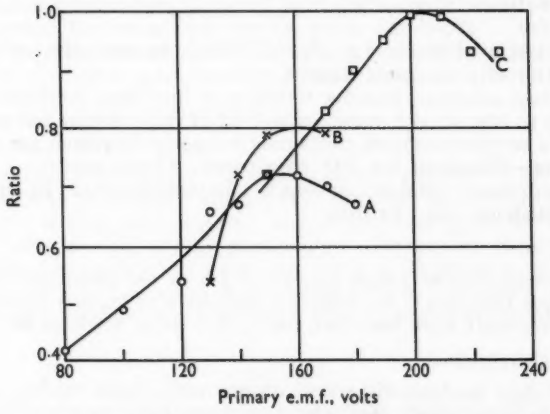

Fig. 2. Ratio of intensities of beryllium line at 3130 A to spectral background plotted against primary voltage for solution containing 0·5 μg of beryllium per ml at different gap widths: curve A, 2 mm; curve B, 3 mm; curve C, 5 mm

knob is raised until the vacuum draws reagent into the space above the stopcock; when the level rises above the tip of the delivery tube the knob is dropped, admitting air around its stem and allowing the excess of reagent to siphon back into the bottle.

It is necessary to control the amount of sulphuric acid used because too much acid prevents precipitation of the calcium phosphate.

SPECTROGRAPHIC DETERMINATION—

The porous-cup technique is used with condensed-spark excitation. The conditions of excitation are selected to give optimum sensitivity with the beryllium line at 3130 A.

The inductance in series with the spark gap is kept to a minimum, because the addition of inductance enhances a hydroxyl band coincident with the beryllium line at 3130 A and thus reduces sensitivity. Another factor affecting the ratio of the intensity of the beryllium line to that of the background is the voltage applied to the primary of the spark transformer. This effect has been studied for three different settings of the spark gap (see Fig. 2), and conditions are chosen to give the highest line to background intensity ratio. A spark gap larger than 5 mm would require an inconveniently high voltage, liable to cause breakdown of insulation.

Gold was chosen as the internal-standard element because of the improbability of its occurrence in air samples and because of the success experienced by Young, Spreadborough and Reid[5] when using it as an internal standard for the porous-cup technique. The gold line at 2913 A has been found suitable and reasonably free from interference by superimposed spectral lines of other elements.

Because of the superimposition of the beryllium and vanadium lines at 3130 A, the electrode material must be carefully selected for freedom from vanadium. Some batches of JM4B graphite, with less than 5 p.p.m. of vanadium, have been found suitable, but the National Carbon Company's "Special Spectroscopic Graphite" is normally used.

It is essential to provide the spark stand of the spectrograph with a hood and extractor fan to withdraw the traces of beryllium fume produced.

METHOD

REAGENTS—

All reagents should be of recognised analytical grade when available.

Sulphuric acid.

Bromine - nitric acid mixture—A saturated solution of bromine in nitric acid.

Calcium phosphate solution—Dissolve 2·5 g of calcium carbonate and 2·5 g of diammonium hydrogen orthophosphate in the minimum amount of dilute hydrochloric acid, and make up to 100 ml with water.

Ammonia solution.

Gold chloride solution—Dissolve 1 g of gold chloride in concentrated hydrochloric acid, and make up to 10 ml with the same reagent.

Standard beryllium solution—Dissolve 0·0983 g of beryllium sulphate, $BeSO_4.4H_2O$, in water, and make up to 100 ml with water; take 1 ml of this solution and make up to 100 ml with water to give a working solution containing 0·5 μg of beryllium per ml.

Sampling papers—Whatman No. 541 filter-paper; 5·5-cm circles.

Envelopes—Transparent cellulose envelopes, non-moistureproof, $2\frac{1}{2}$ inches $\times$ $2\frac{3}{4}$ inches (obtainable from Colodense Ltd., Bristol).

ELECTRODES—

Porous cup—Prepared from $\frac{3}{4}$-inch lengths of $\frac{1}{4}$-inch rod (National Carbon Company's "Special Spectroscopic Graphite") by drilling $\frac{1}{8}$-inch bore to leave a base 0·032 inch thick.

Counter-electrode—Made from the same rod with a point angle of 80°.

SPECTROGRAPHIC CONDITIONS—

Spectrograph—Hilger medium-dispersion quartz with direct-reading attachment.

Source unit—Condensed-spark unit with variable-voltage supply to primary of spark transformer.

Slit width—0·01 mm.

Source to slit distance—33 cm.

Inductance—None added.

Electrode gap—5 mm.

Source input voltage—205 volts.

Exit slits—Set for beryllium line at 3130 A, gold line at 2913 A and background at 3245 A.

Exposure—Controlled by monitoring the gold line at 2913 A so that the spark is cut off at an arbitrary intensity level for this line. The level is chosen to give an exposure time of about 15 seconds, during which most of the solution is consumed.

PROCEDURE—

Place the cellophane envelope containing the filter-paper in the bottom of a 250-ml beaker, and add 1·5 ml of sulphuric acid and 5 ml of bromine - nitric acid mixture. Cover the beaker with a watch-glass, and simmer gently on a hot-plate, avoiding excessive charring. Add further 5-ml portions of bromine - nitric acid mixture as required, until a clear solution is obtained on evaporation to fumes of sulphuric acid.

Set the solution aside to cool, and then dilute carefully with water to about 15 ml. Transfer to a 50-ml centrifuge tube, and add 1 ml of calcium phosphate solution. Add ammonia solution dropwise until precipitation is complete. Spin in a centrifuge for about 3 minutes, and then remove the supernatant liquid. Add about 20 ml of water to wash the precipitate, breaking it up well, again spin in a centrifuge, and remove the liquid as completely as possible.

Dissolve the precipitate in 0·2 ml of gold chloride solution, and transfer, with the minimum amount of water, to a tapered 15-ml centrifuge tube graduated at 1 ml. Make up to 1 ml with water.

Make the graphite cup porous by heating the base for 45 seconds in a blowpipe flame adjusted to raise it to red heat in about 10 seconds. Enough porous cups for one batch of analyses, but not more, should be prepared at one time. Allow the cups to cool before use.

Put the electrodes in position in the holder, and measure 0·1 ml of sample solution into the cup. Set aside for 20 seconds, and then spark the cup under the given conditions.

Measure the intensities of the beryllium line of 3130 A and of the background for each exposure, and subtract to find the true line intensity. Convert the intensity to micrograms of beryllium per millilitre from a working graph.

STANDARDISATION—

Prepare the working graph from standards ranging from 0 to 50 μg of beryllium per ml and covering three different ranges on the instrument. Take each standard through the entire analytical procedure, beginning with a clean envelope and filter-paper, and adding the correct amount of standard beryllium solution before beginning to destroy the organic matter. With each batch of analyses, carry out a test in the same way on both a blank solution and a standard solution containing 0·5 μg of beryllium per ml; this blank and standard are used to standardise the instrument for the particular batch.

If a particular sample contains more than 50 μg of beryllium, bring it within the range of measurement by diluting a small portion of the solution with a suitable amount of the blank solution.

PHOTOGRAPHIC DETERMINATION—

If the photographic method is to be used, reduce the source to slit distance to 30 cm. Use a Kodak B10 plate calibrated with a sector disc and an iron arc. Dilute 2 parts of Ilford ID2 developer with 1 part of water, and develop the plate for 3 minutes at 20° C. Measure the line densities with a microphotometer. Correct the density of the beryllium line at 3130 A for background, and convert the ratio of beryllium to gold line densities to μg of beryllium per ml from a working graph prepared from standards. Correct for a superimposed hydroxyl band at 3130 A by subtracting 0·015 μg from the weight of beryllium found.

RESULTS

The sensitivity of the method has been checked by taking nine successive readings on a blank solution. The average of these was equivalent to 0·003 μg of beryllium per ml. It follows that a sample solution containing 0·015 μg of beryllium per ml can be readily distinguished from the blank. (This corresponds to 0·0015 μg of beryllium present in the 0·1 ml of solution analysed.) A linear working graph is obtained up to 50 μg of beryllium per ml; Fig. 3 shows a typical section of such a graph. The reproducibility of the spectrographic procedure at two points on this curve is shown in Table I.

Table II shows the use of the method for checking the safety of an operation. The specific and the swab samples on day 1 showed that the new operation was creating a local hazard. Checks on day 2 established that this was mainly due to the second part of the operation, and further tests on day 3 showed that modifications to the apparatus had overcome

TABLE I

REPLICATE SPECTROGRAPHIC DETERMINATIONS ON SOLUTIONS OF KNOWN BERYLLIUM CONTENT

Determination No.	Beryllium found in a standard solution containing— 0·2 μg of beryllium per ml, μg per ml	20 μg of beryllium per ml, μg per ml
1	0·201	20·0
2	0·218	21·0
3	0·200	20·4
4	0·202	21·0
5	0·215	19·6
6	0·194	22·0
7	0·187	21·5
8	0·201	18·6
9	—	19·5
Mean	0·202	20·4
Standard deviation	0·010	1·1

the difficulty. Meanwhile, the background samples showed that even at the worst period the beryllium concentration in the general laboratory atmosphere only rose to one-tenth of the maximum permitted average for an 8-hour day.

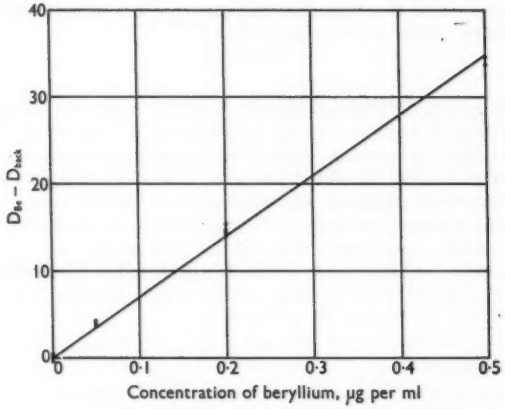

Fig. 3. Typical working graph for determining beryllium with a direct-reading spectrometer (lowest range)

TABLE II

EXAMINATION OF A NEW OPERATION INVOLVING BERYLLIUM

Occasion of sampling	Beryllium found in— background sample, μg per cubic metre	specific sample, μg per cubic metre	swab, μg	exhaust stack sample, μg per cubic metre
Day 1	<0·014	0·6	>50	<0·002
Day 2 First part of operation ..	0·05	<0·02	—	<0·002
Day 2 Second part of operation ..	0·2	1·6	—	
Day 3 (after modification of apparatus)	0·03	0·03	2·7	<0·002

TIME FOR ANALYSIS—

The chemical preparation of four samples takes about 1½ hours and the spectrographic measurement with the direct-reading attachment another 30 minutes. (Photographic

measurement takes about 1 hour longer.) The total time for four samples is thus about 2 hours; the time for twenty samples is about 4½ hours.

Additional Note

Since this paper was prepared for publication the wet-oxidation process has been shortened and made much less troublesome by the use of perchloric acid. Only a single addition of reagent is made to the 250-ml beaker containing the envelope and sample paper; this consists of 0·5 ml of 72 per cent. perchloric acid, 1 ml of sulphuric acid and 5 ml of bromine - nitric acid mixture. The acids are pre-mixed in these proportions, and 6·5 ml of the mixture are added from a single dispenser. A clear solution is obtained in less than 15 minutes, and no modifications to the remainder of the procedure are required.

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Received *October 15th*, 1959

Discussion

Mr. R. A. Hine asked whether the authors had sometimes experienced difficulty owing to clogging of the filter by large amounts of foreign matter. They had tried to determine beryllium in the air around welding plant working on aluminium - magnesium - beryllium alloys, and although they had tried several types of filter, all were choked by the magnesia fumes within 3 or 4 minutes. He asked if electrostatic precipitation had been tried in such circumstances.

Mr. Phennah said that they had never experienced clogging of the filter-paper with the samples taken within the laboratory areas. This was due to the clean conditions necessary for work with beryllium. However, they had experienced clogging of the paper during environmental sampling, particularly in damp and foggy weather. They had not tried electrostatic precipitation.

Mr. W. T. Elwell asked the authors why they had considered it necessary to recover beryllium from the sulphuric acid solution and subsequently examine a chloride solution. It was his considered opinion that adequate sensitivity could be obtained by direct spectrographic examination of the sulphuric acid solution of the sample.

Mr. Powell replied that the direct examination of the sulphuric acid solution by the porous-cup technique would reduce the sensitivity of the method. This was because of the greater viscosity of the acid compared with the chloride solution, which produced a slower rate of flow of the liquid through the base of the electrode. The method they had chosen to overcome this was to recover the beryllium from the sulphuric acid.

Mr. Elwell stated that the method of spectrographic examination in which the porous-cup technique was used was not the only one available (the implication was that the sulphuric acid solution could be examined directly by using other types of electrode, such as a polythene cup).

Mr. J. F. W. Smith asked if there was any particular reason for using the unusual type of air sampler illustrated, since commercial samplers were available that did not need constant supervision. This was necessary with the type described by the authors if an accurate measure of the volume of air was required. Calculations based on pumping speed would not be valid for atmospheres in which the paper was likely to clog.

Mr. Phennah explained that the type of air sampler illustrated had been used because it was cheap, reliable, compact and sufficiently flexible to accommodate the type of air sampling that was carried out within the laboratory areas. They did in fact use the commercially available instruments for environmental sampling where constant supervision would be uneconomical. With regard to the accuracy with which the volume of air passed was measured, he thought he was correct in saying that even the commercially available instruments required a special calibration if this measurement was to be carried out with high precision.

Dr. G. W. C. Milner asked the authors if they had had any experience with their technique when the beryllium metal was contaminated with beryllium oxide.

Mr. Powell replied that their experience had been limited to the determination of beryllium metal in air. However, it ought to be possible by this method to determine beryllium present in other forms, provided they were taken into solution by the chemical procedure.

MR. T. R. ANDREW enquired if the authors had had any experience with the use of Millipore filters, for which the retention of very fine particles, combined with non-clogging properties, are claimed.

MR. PHENNAH replied that they were interested in the use of Millipore filters, or high-efficiency filters of that type, but they had had no experience in their use so far.

MR. A. E. HERON mentioned the speaker's statement that 20 determinations could be made in 4½ hours. He wished to know the minimum time in which a single determination could be made.

MR. POWELL said that time required for a single determination was a little under 2 hours.

MR. R. H. A. CRAWLEY referred to Mr. Andrew's question and said that at the English Electric Co. they had had considerable experience with German membrane filters of a type equivalent to the American Millipore filter, and found that they had superior properties to Whatman filter-paper for air filtration. A membrane filter equivalent to Whatman No. 41 or No. 541 filter-paper in terms of air flow would retain all particles greater than 0·5 μ, whereas a considerable proportion of particles in the range 0·5 to 2·0 μ would pass through the filter-papers. This was just the range of particle sizes thought to be most hazardous in causing berylliosis. Another advantage of membrane filters was that they did not clog so rapidly as filter-paper in dirty atmospheres.

He then asked if the authors would comment on "smear" sampling, particularly as to whether they considered that that type of sampling gave valuable information or that it could be used instead of air sampling in routine monitoring operations.

MR. PHENNAH replied that they were very interested in Mr. Crawley's remarks on membrane filters and would welcome further information.

Their attitude to smear (or swab) sampling was that the technique did not provide a substitute for air sampling. However, it did provide valuable information about the degree of surface contamination, which was necessary in order to establish whether or not sufficient control was being exercised.

MR. T. MCLACHLAN asked whether the authors had ever attempted to determine the amount of beryllium passing the filter-paper by drawing the air through sulphuric acid or some other solvent after it had passed through the filter-paper.

MR. PHENNAH said that they had not attempted this.

DR. J. C. GAGE asked what was the average sampling time required for measuring the limit of 2 μg of beryllium per cubic metre of air. As it had been laid down that the concentration should not at any time exceed 25 μg per cubic metre, it seemed possible that if the sampling lasted for several hours, an occasional peak above this limit might be missed.

MR. PHENNAH replied that the chemical procedure finally produced a solution containing all the beryllium in a volume of 1 ml. One-tenth of this volume was used for the spectrographic determination, with a sensitivity of 0·015 μg of beryllium per ml. If it was assumed that an air sample was taken from an area in which the beryllium concentration was 2 μg per cubic metre with a sampling device that drew air at the rate of 10 litres per minute, then the duration of sampling had to be 75 minutes in order to provide the spectroscopist with a detectable amount of beryllium. At their Erith laboratory, specific samples were taken for a duration of 1 to 4 hours. They considered that this was a sufficient duration to ensure adequate sensitivity without the danger of obscuring an occasional spurious release by means of the effective dilution that resulted from high sampling rates.

An instantaneous-response monitor was obviously necessary for the satisfactory detection of a spurious release of beryllium that exceeded the absolute maximum permitted level of 25 μg per cubic metre. A number of specific air samples taken within the laboratory at Erith had been reported to contain concentrations of beryllium which, when related to the volume of air passed, gave an average concentration that approached or exceeded 2 μg per cubic metre. They interpreted such results in terms of one or more spurious releases of beryllium rather than as the result of sampling from air of constant beryllium concentration. On the receipt of such a result they therefore investigated the particular operation in order to identify the cause of the spurious release. As an example, by carrying out a special air-sample survey of their machining operations, they found that the high-velocity air-extraction technique provided adequate safety during the machining, but was ineffective in preventing spurious releases during transfer operations from the ventilated lathe box.

The Determination of Nitrofurazone in Feed Mixes

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A method has been developed for determining low concentrations (~0·01 per cent.) of nitrofurazone in feed mixes. The active medicament is extracted from the feed after partial removal of interfering substances. The optical density of the mauve colour subsequently developed in an alkaline solution of the nitrofurazone in NN-dimethylformamide is measured in a suitable spectrophotometer at 5300 A.

The reports by Dodd and Stillman[1,2] that nitrofurazone (5-nitrofurfurylidene semicarbazone) possessed pronounced antimicrobial properties have led to its use in the prophylactic and curative treatment of caecal coccidiosis in poultry[3,4] and in the treatment of pigs,[5] cattle,[6] sheep[7] and rabbits.[8] A monograph on nitrofurazone was included in the 1953 edition of the British Veterinary Codex[9]; its use was described for the treatment of avian coccidiosis, in which the drug levels are about 0·005 to 0·02 per cent. of the feed. This paper describes our attempts to develop an analytical technique capable of providing reasonably accurate results at such concentrations of nitrofurazone.

Ells, McKay and Paul[10] described a simple ethanolic-extraction method for separating the nitrofurazone from medicated feeds, and their technique was later modified by Buzard, Ells and Paul,[11] who preferred to extract at 55° to 60° C, with mechanical agitation. Dixon[12] preferred either methanol or acetone as extraction medium, and van Zijl and Goossens[13] used acetone because it easily extracted nitrofurazone at room temperature. In a method described as the "Microdetermination of the Medicaments Furazolidone and Nitrofurazone," Beckman[14] advocated the use of NN-dimethylformamide as solvent.

From our experience with the various nitrofurazone-containing feeds available in recent years, it seems that previous workers were probably concerned with de-fatted or natural cereals and inert inorganic diluents or both. The introduction of grass meal into the feed and the incorporation of synthetic chemicals has generally rendered simple extraction methods valueless.

Kawashiro and Fukuzawa[15] attempted to remove interfering substances by pre-treatment of the feed with a solvent in which the nitrofurazone was insoluble, *e.g.*, light petroleum. Ells, McKay and Paul recommended the use of light petroleum, carbon tetrachloride or a mixture of these solvents,[10] but Dixon[12] reported that the final ethanolic solution still contained sufficient yellow-green pigment to interfere with the subsequent spectrophotometric assay. On the supposition that the nitrofurans would be insoluble in saturated hydrocarbons, pre-treatment of the feed with Skellysolve B was suggested in a personal communication from Mr. L. R. Stone (Hess and Clark Inc., Ashland, Ohio, U.S.A.).

Analytical procedures involving direct-extraction or pre-treatment methods are likely to result in relatively high blank values or in high recoveries of apparent nitrofurazone, and Buzard, Ells and Paul have attempted to decrease the blank effect by reducing the yellow nitrofurazone in the blank solution to a colourless compound by means of sodium dithionite.[11] van Zijl and Goossens[13] removed much of the interfering products by an oxidation process, but in our laboratories this method gave variable recoveries, as excessive amounts of potassium permanganate decomposed the nitrofurazone.

The unsatisfactory extraction procedures prompted investigators in this field to apply chromatographic-separation techniques, and Dixon[12] described a paper-chromatographic method in which Whatman No. 3 MM paper in a chloroform - *iso*propyl alcohol - potassium benzoate solvent was used. As we found great difficulty in applying this technique, some experiments were made with a two-dimensional paper-chromatographic method, but without success. Beckman,[14] in his study of furazolidone - nitrofurazone mixtures, used an alumina column and a solution of the nitrofurans in NN-dimethylformamide. Under these conditions the nitrofurazone was retained as a distinct orange-red band just below the surface of the alumina column.

Although a wide variety of procedures has been put forward for recovering nitrofurazone from medicated feed mixes, the final method of determination has generally been based on spectrophotometric absorption measurements against standard solutions of nitrofurazone.

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TABLE I

EFFECT OF PHENOL ON OPTICAL DENSITIES OF ALKALINE SOLUTIONS OF NITROFURAZONE IN DIMETHYLFORMAMIDE

Each solution contained 0·1 g of sodium hydroxide

Amount of phenol present, g	Initial optical density	Optical density after—		
		30 minutes	90 minutes	19 hours
Solutions stored in dark—				
Nil	0·455	0·424	0·420	0·355
0·25	0·598	0·600	0·597	0·598
0·25	0·596	0·597	0·598	0·599
Solutions stored in light—				
Nil	0·478	0·407	0·386	0·267
0·25	0·599	0·589	0·570	0·548
0·25	0·588	0·588	0·575	0·535

Since the final extract is usually pale yellow or yellow tinged with green or brown, attempts have been made to intensify the colour produced by the nitrofurazone and so to increase the value of instrumental measurements. Tagaki and Uno[16] proposed the addition of caustic alkali to solutions of nitrofurazone, a method also favoured by Kawashiro and Fukuzawa,[15] Shibazaki and Terui[17] and Thompson.[18] We have shown that the orange-red colour is unstable, and such methods are unsuitable for quantitative work.

The reaction between phenylhydrazine and hydrolysed nitrofurazone to produce a bright red product has been used by Buzard, Ells and Paul,[11] Stone (described in the personal communication mentioned above), Flach[19] and Puglisi,[20] but the results in Flach's and Puglisi's reports—which cover collaborative assays—clearly indicate the inadequacy of the method.

Nagasawa and Okhuma[21] proposed a gravimetric determination of nitrofurazone as its 2:4-dinitrophenylhydrazone, but the method has not proved successful when applied to poultry feeds.

In work on the determination of certain aromatic nitro compounds, Porter[22] studied the colour reactions applicable to such determinations and particularly the reaction with tetraethylammonium hydroxide in a solution of the nitro compound in dimethylformamide. This reaction was subsequently applied by Freeman[23] to the determination of chloramphenicol, which has a *para* nitro group.

EXPERIMENTAL

Although dimethylformamide is a useful solvent for nitrofurazone and of possible value in colorimetric determinations, it was found that the addition of aqueous or alcoholic alkali to such solutions resulted in unstable mixtures of little value in quantitative work. The intensity of the colour produced indicated its potential value for spectrophotometric measurements, but the reaction mixture needed to be stabilised before it could be used on a quantitative basis. Of the many compounds tested, only a few had any colour-stabilising effect, but phenol provided adequate protection during the time required for carrying out a determination.

The effects of phenol, sodium hydroxide and water on colour formation and stability were studied, and typical optical-density measurements made with a Uvispek spectrophotometer are shown in Tables I, II and III. These results show that fairly strict control of the concentrations of sodium hydroxide, phenol and water could lead to mixtures suitable for quantitative determinations of nitrofurazone.

TABLE II

EFFECT OF VARIATION IN AMOUNTS OF WATER AND PHENOL PRESENT

Each solution contained 0·1 g of sodium hydroxide

Amount of phenol present, g	Amount of water present, ml	Initial optical density	Optical density after—	
			90 minutes	19 hours
Nil	7·5	0·188	0·130	Colourless
0·25	2·5	0·388	0·388	0·385
	3·5	0·365	0·365	0·362
	4·5	0·340	0·340	0·340
	7·5	0·285	0·285	0·207
	12·5	0·200	0·175	0·038

TABLE III

EFFECT OF VARIATION IN AMOUNTS OF WATER AND SODIUM HYDROXIDE PRESENT

Each solution contained a constant amount of phenol

Amount of sodium hydroxide present, g	Amount of water present, ml	Initial optical density	Optical density after—		
			90 minutes	150 minutes	19 hours
0·029	0·10	0·067	0·207	0·285	0·306
0·102	0·35	0·209	0·388	0·435	0·418
0·142	0·50	0·242	0·372	0·382	0·348
0·293	1·00	0·306	0·372	0·379	0·305
0·732	2·5	0·316	0·347	0·347	0·138
0·100	2·5	0·388	0·388	0·388	0·395

The general method used is described below—

Dissolve the nitrofurazone recovered from the feed mix in dimethylformamide to provide a solution containing about 0·1 mg of nitrofurazone per 10 ml. To each 10 ml of this solution add 2·5 ml of *N* aqueous sodium hydroxide and 5 ml of a 5 per cent. w/v solution of phenol in dimethylformamide.

This method was applied to various poultry feeds, which were of two main types. With the first type, designated "simple," no obvious difficulties were experienced during the determination and blank values were relatively small. The second type, designated "complex," contained grass meal and other chemical supplements in addition to the usual cereal and inorganic diluents. Typical results are shown in Table IV.

TABLE IV

RECOVERY OF ADDED NITROFURAZONE FROM POULTRY FEED MIXES

Type of feed	Nitrofurazone added, mg	Nitrofurazone found, mg	Recovery, %
Simple	0·589	0·57	97
	1·050	1·06	101
	1·204	1·19	99
	1·807	1·80	100
	2·510	2·46	98
	3·080	3·06	99
	3·810	3·80	100
Complex (5 per cent. of grass meal)	0·498	0·632	127
	0·991	1·139	114
Complex (10 per cent. of grass meal)	0·640	0·800	125
	1·062	1·306	123
	4·972	5·206	105
Complex (other additives)	0·468	0·438	94
	0·988	0·853	96
	1·025	0·883	86

Although the results for "simple" feeds were satisfactory, recoveries from "complex" feeds were less so. For the recoveries in excess of 100 per cent., the error probably arose from the co-extraction of materials having anomalous absorption. When the recovery values were substantially less than 100 per cent., the errors were possibly caused by high blank values or by reduction of nitrofurazone during the determination.

The presence of reducing compounds in some of the "complex" feeds was confirmed by a study of the absorption characteristics at different periods of time. For example, when a solution containing 0·93 mg of nitrofurazone was tested by the normal procedure, and the optical density was measured after 30 minutes with a Uvispek spectrophotometer, only 92 per cent. of the nitrofurazone present was found; the recovery was further reduced to 72 per cent. when the optical density was measured after 2 hours.

Such results made it necessary to develop a method that would destroy any reducing compounds present and would also lead to low blank values.

At this stage, our results had been communicated to and discussed by the Prophylactics Panel of the Analytical Methods Committee of the Society for Analytical Chemistry, which was set up to consider the determination of such additives in animal feeding stuffs. Members of this Panel encountered similar difficulties, and we considered the use of van Zijl and Goossen's oxidation method.[13] This we decided to modify by using only sufficient dilute potassium permanganate solution to give a slight excess in the concentrated solution of nitrofurazone in acetone. The results are shown in Table V.

TABLE V

RECOVERY OF ADDED NITROFURAZONE FROM "COMPLEX" FEEDS

	Nitrofurazone added, mg	Nitrofurazone found when optical density was measured after—	
		30 minutes, mg	2 hours, mg
Potassium permanganate absent ..	0·939	0·86	0·675
Potassium permanganate present ..	1·028	1·042	1·050
	1·002	1·012	—
	1·009	1·009	1·009

For a few samples the oxidation technique alone did not always give satisfactory recoveries, and these errors were attributed to the higher blank values. Buzard, Ells and Paul[11] had earlier commented on this and had recommended the use of a modified blank solution prepared by treating the nitrofurazone extract with sodium dithionite.

Our results confirmed the better recovery of nitrofurazone when such a modified blank solution was used, and the use of sodium dithionite became standard procedure in our subsequent work. The method finally adopted involves (*a*) pre-extraction of the feed, (*b*) extraction of the nitrofurazone, (*c*) oxidation of interfering material, (*d*) development of a stable and highly intense colour, (*e*) preparation of a modified blank solution and (*f*) measurement of the optical density of the colour with a Uvispek spectrophotometer.

METHOD

PROCEDURE—

Carefully weigh 10 g of feed or an amount containing about 1 mg of nitrofurazone into a Whatman extraction thimble, and place a small pledget of cotton-wool on the surface of the feed, which should not be pressed down into the thimble. Extract with light petroleum (boiling range 40° to 60° C) in a Soxhlet apparatus for about 30 minutes, during which time the solvent should have completed fifteen cycles. (An Electrothermal mantle or similar equipment is a suitable source of heat.) Remove the thimble, and allow the solvent to drain away. When dry, re-extract in the Soxhlet apparatus with carbon tetrachloride for 30 minutes or until the solvent has completed fifteen cycles. Remove the thimble, allow the solvent to drain, and dry the residue in the thimble in a current of warm air. Transfer to a clean Soxhlet apparatus, and extract with acetone for 1 hour or until the solvent has completed twenty cycles (use a steam-bath as the source of heat). It is advisable to protect the apparatus from light at this stage, as the nitrofurazone is photosensitive. When extraction is complete, carefully remove most of the acetone, still protecting the apparatus from light. Cool the remaining 5 ml of acetone extract to room temperature, and add 0·1 *N* potassium permanganate until a faint pink colour is obtained (3 drops or less will usually suffice). Carefully remove the remainder of the acetone by warming on the steam-bath in a current of warm air. Dissolve the yellowish residue in NN-dimethylformamide, quantitatively transfer the solution to a 50-ml calibrated flask, and dilute to the mark with NN-dimethylformamide at 20° C. Transfer an aliquot containing about 0·05 to 0·35 mg of nitrofurazone to each of two 50-ml calibrated flasks, and add 5 ml of a 5 per cent. w/v solution of phenol in NN-dimethylformamide to each.

To the contents of one flask add 2·5 ml of *N* aqueous sodium hydroxide, and dilute to the mark with NN-dimethylformamide; this is the sample solution. To the contents of the other flask add 2·5 ml of a freshly prepared 1 per cent. solution of sodium dithionite in *N* aqueous sodium hydroxide, and dilute to the mark with NN-dimethylformamide; this is the blank solution.

Set the solutions aside for 5 minutes, and then spin them in a centrifuge for 2 minutes at 6000 to 10,000 r.p.m. and 6-cm radius. Measure the optical density of the sample solution

against the blank in 1-cm cells at 5300 A with a Uvispek spectrophotometer, and calculate the amount of nitrofurazone present in the extract dilution and hence in the feed from a calibration graph prepared by plotting the optical densities obtained when known amounts of nitrofurazone are treated as described above.

Results

The proposed method was applied to the recovery of added nitrofurazone from a series of 10-g samples of prepared "complex" feed mixes containing grass meal and other ration supplements. The results were—

Nitrofurazone added, mg	.. ..	0·503	0·640	1·015	1·027	1·995
Nitrofurazone found, mg	.. ..	0·502	0·650	1·009	1·041	1·980
Recovery, %		100	101·5	99·5	101·5	99

The method was also applied to a few commercially available feed mixes containing nitrofurazone; recoveries were between 98 and 102 per cent. of the declared nitrofurazone concentrations.

The method has been submitted to the members of the Prophylactics Panel of the Analytical Methods Committee, and a collaborative investigation is being made.

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The Determination of Phenothiazine in Commercial Preparations by Chromatography

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A chromatographic method is described; it has been successfully applied to the analysis of commercial crude samples of phenothiazine and dust and dispersion formulations. The method involves the use of a mixed adsorbent consisting of equal parts by weight of silicic acid and Magnesol. Addition to the adsorbent of approximately 3 per cent. by weight of freshly precipitated copper prevents oxidation during the separation and also immobilises hydrogen sulphide and sulphur. A mixture of methylene chloride and *n*-hexane is used for elution.

THE work described in this paper was undertaken in an attempt to resolve the difficulties encountered in the analysis of phenothiazine preparations.

The colorimetric bromine method,[1] based on work by Eddy and de Eds[2] and Cupples,[3] was tried, but was found to be sensitive to small variations in technique. The colorimetric procedure described by Overholser and Yoe[4] produces unstable colours, and Kniaseff's method[5] is time-consuming. Oxidation of phenothiazine by ferric chloride or hydrogen peroxide under different conditions, extraction with *n*-butyl alcohol and then measuring the colour produced at 506 mμ with a spectrophotometer also failed to give consistent results. Essermann's paper-chromatographic method,[6] although useful for work on residues, is unsuitable for the analysis of commercial samples.

EXPERIMENTAL

Preliminary tests on alumina columns with toluene as eluting agent indicated the need for a more specific and powerful adsorbent. Gradient elution with benzene in light petroleum from a column of silica gel required too much attention, and noticeable oxidation resulted in incomplete recoveries. Prevention of oxidation by means of an aqueous solution of hydrazine sulphate was unsuccessful.

Because the oxidation of phenothiazine is more pronounced in acid conditions, a more neutral adsorbent and a more powerful oxidation preventive were desirable. A column consisting of equal amounts of silica gel and a basic adsorbent, Magnesol (a synthetic magnesium silicate, similar in adsorption characteristics to silica gel), was tested, a 10 per cent. v/v solution of methylene chloride in light petroleum, boiling range 40° to 60° C, being used as eluting agent. The mixture of solids was introduced into the chromatographic tube in the form of a slurry with the eluting agent; before the mixture had settled, the slurry was purged with nitrogen. Hydrogen sulphide was introduced into the eluting agent to prevent oxidation of phenothiazine during chromatography. Although, for mixtures of the two substances, sulphur is eluted before phenothiazine, it was found that if the eluting agent contained elemental sulphur, produced by oxidation of the hydrogen sulphide, the phenothiazine was contaminated and the results of the analyses were high. At this stage, two ways of approach were possible—either to determine the amount of elemental sulphur mixed with the eluted phenothiazine and to apply a correction or to prevent oxidation of the phenothiazine during separation by some other means.

Two methods for determining elemental sulphur were tried; only one[7] was applicable in the presence of phenothiazine, although the errors involved were large. It seemed that any method depending on the reduction of sulphur and evolution of hydrogen sulphide could not be used, as phenothiazine formed hydrogen sulphide with the reducing reagents tried, *e.g.*, zinc dust in acetic acid and a mixture of hydriodic and hypophosphorous acids.

The addition to the adsorbent of freshly precipitated copper as antioxidant was satisfactory. Further, it immobilised unreacted sulphur and also hydrogen sulphide present in some phenothiazine samples.

Several factors affecting the separation of phenothiazine from accompanying impurities were investigated.

SOLVENT COMPOSITION—

The system methylene chloride - *n*-hexane was tested in the range 5 to 20 per cent. v/v of methylene chloride. The criterion was the separation of phenothiazine from added diphenylamine, which immediately preceded the phenothiazine band. It was found that 15 per cent. v/v was the tolerable upper limit for the concentration of methylene chloride. Although it resulted in a somewhat longer period of elution, 10 per cent. v/v of methylene chloride in *n*-hexane was chosen for ease in detecting separation.

EFFECT OF MOISTURE CONTENT OF ADSORBENTS—

Silica gel and Magnesol were dried at 200° C for 3 hours. A series of mixtures was then prepared, and water was added to each to give a range of water contents from 6 to 14 per cent. w/w of the dry adsorbent mixture. It was found that, as the water content was increased, a shorter period of elution and a smaller volume of eluting agent were needed before the phenothiazine band appeared. The width of the band was not affected, and the separation from neighbouring bands was not significantly altered. The limit to water content is set by the effect on the mechanical characteristics of packing. Because a slight discoloration of Magnesol was noticed when it was dried at 200° C, I prefer to dry only the silica gel (at 400° C) and to use undried Magnesol (moisture content determined at 200° C varies between 20 and 20·5 per cent. w/w); no extra water is then required.

EFFECT OF AMOUNT OF COPPER POWDER IN ADSORBENT MIXTURE—

The copper in the adsorbent mixture, apart from its reaction with oxygen, sulphur and hydrogen sulphide, has a retarding action on the appearance of the bands and does not appreciably improve their separation. A ratio of about 1 g of copper to 30 g of silica gel - Magnesol mixture was considered to give a safe margin, without unnecessarily extending the duration of elution.

METHOD

APPARATUS—

Chromatographic tube—The dimensions of the chromatographic tube are shown in Fig. 1. The temperature of the cold water should be between 14° and 16° C; it should not exceed 18° C.

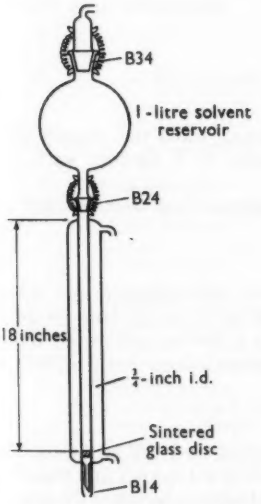

Fig. 1. Chromatographic tube

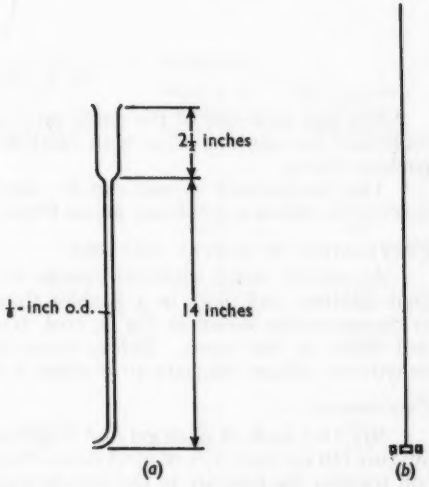

Fig. 2. (*a*) Delivery tube; (*b*) packing disc

Delivery tube—The dimensions of the tube used for placing the sample on the column are shown in Fig. 2 (*a*).

Perforated packing disc—The packing disc is shown diagrammatically in Fig. 2 (*b*). It is $\frac{5}{8}$ inch in diameter and $\frac{1}{16}$ inch thick and has six holes, each $\frac{1}{16}$ inch in diameter. The disc is attached to a rod $\frac{1}{8}$ inch in diameter and 2 feet 6 inches long.

PREPARATION AND PRESERVATION OF COPPER POWDER—

Dissolve 45 g of analytical-reagent grade cupric sulphate crystals in 500 ml of cold distilled water containing 20 ml of 2 *N* hydrochloric acid (analytical-reagent grade). Prepare a thick slurry of 15 g of analytical-reagent grade zinc powder in 25 ml of water containing a small amount of Lissapol N, and slowly add the copper sulphate solution from a separating funnel. Maintain rapid mechanical agitation during the addition. Continue to stir until the precipitated copper assumes a red to red-brown colour. Decant the supernatant liquid, and allow some of the finer particles of precipitate to be removed. Repeatedly wash the copper with freshly distilled water and then with acetone, and press it between pieces of filter-paper. Weigh on a rough balance 1 g of copper into each compartment of a plastic ice-cube tray, cover with water, and freeze from the top (otherwise the copper will be pushed to the surface of the cubes).

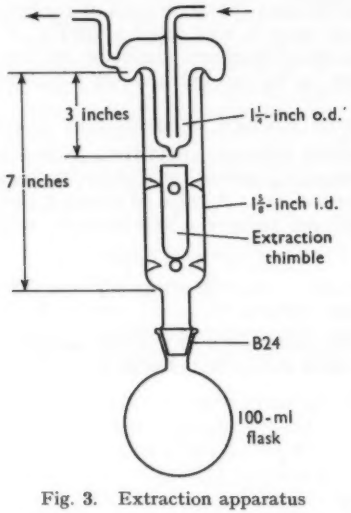

Fig. 3. Extraction apparatus

For use, melt one of the cubes on a small sintered-glass funnel, wash the copper with redistilled acetone and then with methylene chloride, and transfer to a blender with the packing slurry.

The precipitated copper can be used immediately after preparation, but is said to deteriorate within a few hours unless frozen in ice.[8]

PREPARATION OF SAMPLE SOLUTION—

Accurately weigh sufficient sample to provide 25 to 30 mg of phenothiazine per ml of final solution, and place in a Soxhlet thimble. Extract with 50 ml of methylene chloride in the apparatus shown in Fig. 3, cool, transfer quantitatively to a 100-ml calibrated flask, and dilute to the mark. Before extraction, mix dispersion formulations with sufficient anhydrous sodium sulphate to produce a dry powder.

PROCEDURE—

Mix 15 g each of silica gel and Magnesol (see Note), 1 g of copper and 120 ml of solvent mixture (10 per cent. v/v of methylene chloride and 90 per cent. v/v of *n*-hexane) in a blender, and transfer the mixture to the chromatographic tube. Remove trapped bubbles by means of the perforated disc, introducing it to the bottom of the column and moving it upwards

with a slow rotatory motion. Connect the top of the column to a cylinder of nitrogen via a manometer and mercury lute, and apply pressure of approximately 1 lb per sq. inch until the level of solvent is just above the level of the column of adsorbent. Release the pressure, and introduce 2 ml of sample solution by using the delivery tube. Rinse with a little methylene chloride (0·5 ml) from a dropper, and again apply pressure. Rinse the sides of the chromatographic tube twice with solvent mixture, and force each washing down individually. In no circumstances should the packing be allowed to get dry. Connect the reservoir, and elute with 800 ml of solvent mixture, applying pressure of nitrogen to give a suitable rate of flow (normally 1·5 to 2 ml per minute at a pressure of about 5 to 6 lb per sq. inch). Collect 10-ml fractions. Evaporate the solvent from each fraction individually in a water bath at about 30° to 35° C and under reduced pressure. (Multiple-evaporation adaptors and controlled shaking are an advantage[9]; a visual inspection reveals the boundaries of the phenothiazine band.) Rinse the phenothiazine-containing fractions into a tared flask with methylene chloride. Remove the methylene chloride by evaporation, dry at 100° C for about 30 minutes, and allow to cool in a vacuum desiccator.

NOTE—The production of Magnesol (formerly marketed by the Westvaco Chemical Corporation, New York, U.S.A.) has now been abandoned, and the use of the manufacturer's recommended substitute, Sea Sorb 43, of magnesium trisilicate and of magnesium oxide was unsuccessful. A suitable substitute, not so good as Magnesol, but reasonably satisfactory, is 200- to 300-mesh Florisil, obtainable from the Floridin Company Inc., Tallahassee, Florida, U.S.A.

RESULTS

Samples of purified phenothiazine were treated as described above; the results were—

Recovery, %	99·0	99·3	99·6	99·0	99·2	99·4
Melting-point of recovered material, °C ..	184 to 185	185	185	185	185	184 to 185

Prepared mixtures of phenothiazine and a variety of impurities and formulating agents known to be present in commercial preparations were analysed by the proposed method; the results are shown in Table I. The amounts of phenothiazine found in various types of commercial preparations, the phenothiazine contents of which were not disclosed, are shown in Table II. The melting-points of the recovered-phenothiazine fractions were determined with a Kofler hot stage. All commercial samples were of Australian origin; formulations contained surface-active agents, diluents, etc., and the liquid formulations were dispersions in water.

CONCLUSIONS

The method described has been successfully applied to the analysis of commercial samples of phenothiazine. The figures in Table II are typical of the replicate results usually

TABLE I

RECOVERY OF PHENOTHIAZINE FROM PREPARED MIXTURES

Mixture No.	Compound	Weight of compound present, mg	Weight of phenothiazine in sample used, mg	Weight of phenothiazine recovered, mg	Melting-point of recovered phenothiazine, °C
1	Phenothiazine ..	1619	64·8	64·6	184
	Phenothiazine-5-oxide	101		64·7	185
	Phenothiazone-3 ..	96		64·3	185
	Thionol	132			
	Diphenylamine ..	8			
2	Phenothiazine ..	1302	52·1	52·0	184
	Phenothiazine-5-oxide	77		51·8	184
	Phenothiazone-3 ..	66		51·8	185
	Thionol	50			
	Volclay	203			
3	Phenothiazine ..	1505	60·2	60·2	184
	Phenothiazine-5-oxide	55		60·1	185
	Phenothiazone-3 ..	55		60·0	184
	Thionol	53			
	Totanin*	103			
	Manucol	24			
	Bentonite	32			

* Present as a 32 per cent. w/v solution.

TABLE II

AMOUNTS OF PHENOTHIAZINE FOUND IN COMMERCIAL SAMPLES

Sample designation	Phenothiazine found, %	Melting-point of phenothiazine fraction, °C
Dispersion formulation NLP	42·7	
	42·1	
	42·6	
Dispersion formulation CRF859	40·2	
	40·5	
	40·3	
Powder formulation PS473	67·5	
	68·3	
	68·1	
Micronized crude RF434	84·0	
	83·6	184 to 185
	83·4	
Crude BB2MF	86·4	
	86·7	
	87·0	
Crude BB3MF	82·1	
	82·5	
	82·7	
Crude BB570 CIG	93·5	
	93·2	
	93·3	

obtained. The accuracy of the method is better than those of the colorimetric procedures and is independent of subjective variations. Scaling up the method to permit the use of larger weights of sample has not so far proved practicable, the difficulty being mainly in the nature of phenothiazine, which has low density and sputters excessively when the last traces of solvent are removed from bulky deposits. The handling of 50 to 60 mg of phenothiazine, however, offers no difficulties. The method is of general application to the analysis of all commercial forms of phenothiazine so far encountered.

I thank Imperial Chemical Industries of Australia and New Zealand Ltd. for permission to publish this paper.

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A Possible Use of Ammonium 12-Molybdophosphate for Assaying Certain Radioactive Fission Products in Water

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Many cations, including those of caesium-137/barium-137*m*, strontium-90/yttrium-90 and cerium-144/praseodymium-144, are efficiently removed from neutral solution by a pre-formed precipitate of ammonium 12-molybdophosphate supported on a filter-paper in a de-mountable funnel. Caesium is selectively taken up by this compound from dilute nitric acid solution, and a method based on this fact is suggested for the quantitative determination of radioactive caesium.

The assay of trace amounts of radioactive material in water is not normally an easy task. The determination is often confined to one of total radioactivity; the sample is evaporated to dryness, the residue (ashed if necessary) is counted with an end-window Geiger tube, and, after allowance has been made for the activity of any potassium present, the result is expressed in terms of the most hazardous nuclide suspected. This procedure is, however, not always adequate, and a more detailed assay may be required.

The general principles involved in the assay of a particular radioactive nuclide are the addition of a known amount of an isotopic carrier (if possible), recovery of this carrier together with the activity to be determined, removal of radioactive impurities by scavenging, determination of the recovery of the carrier and measurement of the activity. This procedure is often difficult and tedious, especially when a small amount of activity is present in a large volume of sample.

A possible method for concentrating small amounts of radioactivity is by ion exchange, and much work has been carried out in this direction. A disadvantage of the procedure is, however, that the column of ion-exchange resin must be large enough to adsorb other elements, which may be present in considerable excess, as well as the radioactive nuclides being assayed. For example, a column able to adsorb the calcium, magnesium and alkali metals in a large volume of natural water may be inconveniently large for the subsequent elution of any strontium-90 and caesium-137 present. Complexing agents may sometimes be used to decrease or even remove such interference and so make the ion-exchange resin more specific. For example, at pH 5·5 in presence of ethylenediaminetetra-acetic acid (EDTA) strontium is quantitatively retained on a column of Zeo-Karb 225, whereas calcium is complexed and passes through; much smaller ion-exchange columns are therefore required for separating and concentrating strontium-90.[1]

Experimental

Use of ammonium 12-molybdophosphate—

A similar increase in specificity could be obtained without the use of complexing agents by choosing an ion-exchange material efficient only for the elements it is desired to concentrate. Buchwald and Thistlethwaite[2] have shown that, in dilute nitric acid solution, ammonium 12-molybdophosphate readily exchanges ammonium for potassium, rubidium, caesium and thallous ions, but hardly at all for lithium, sodium, calcium, strontium and barium ions. Smit has demonstrated the considerable selectivity of this compound for caesium,[3] and Smit, Robb and Jacobs have recently shown that certain multivalent ions are readily removed from neutral solution.[4]

Since ammonium 12-molybdophosphate is so efficient in removing sub-microgram amounts of certain fission-product cations from solution under the correct conditions, it was thought worth while to support the compound on filter-paper in a 1-inch diameter de-mountable Buchner funnel and to ascertain whether or not merely pouring a labelled solution through the filter would suffice to remove the activity. We found that this treatment quantitatively removed caesium from neutral or dilute nitric acid solution and trace concentrations of all other elements so far examined from neutral solution (see Table I, p. 368).

These elements are listed below, the tracer used being shown in brackets—

Strontium (^{89}Sr), barium (^{140}Ba), lanthanum (^{140}La, the daughter of ^{140}Ba), cerium (^{144}Ce), scandium (^{46}Sc) and yttrium (^{91}Y).

The last-named element is, of course, important in connection with the assay of strontium-90, the daughter of which is the radioactive nuclide yttrium-90.

Unfortunately, from the point of view of water analysis, although there is little interference with the removal of caesium from acid solution, except perhaps by thallous ions (see Table II, p. 368), the presence of calcium seriously reduces the efficiency with which strontium is concentrated (see Fig. 2, p. 369). This interference is reduced only slightly, if at all, by adding EDTA, and it is interesting to compare this observation with that of Davis,[1] who found that, with proper choice of pH and in presence of EDTA, calcium ions did not interfere with the removal of strontium ions from solution by Zeo-Karb 225.

CAPACITY OF AMMONIUM 12-MOLYBDOPHOSPHATE—

If ammonium 12-molybdophosphate is to be used to remove microgram amounts of radioactive nuclides from solution for assay purposes, the efficiency of the process is more important than the maximum capacity of the material. Nevertheless, it is of interest to determine approximately how much of the various cations can be taken up by a given amount of molybdophosphate. We carried out this determination in neutral solution for caesium, strontium and yttrium by preparing solutions containing different concentrations of each labelled cation and treating them as described under "Procedure." The capacity was calculated from the expression—

$$\text{Capacity, equivalents per mole of molybdophosphate} = \frac{E \times \text{Equivalents of cation used} \times 1880}{100 \times 120 \times 10^{-3}},$$

in which E is the percentage efficiency of removal and it is assumed that the molecular weight of ammonium 12-molybdophosphate is 1880.

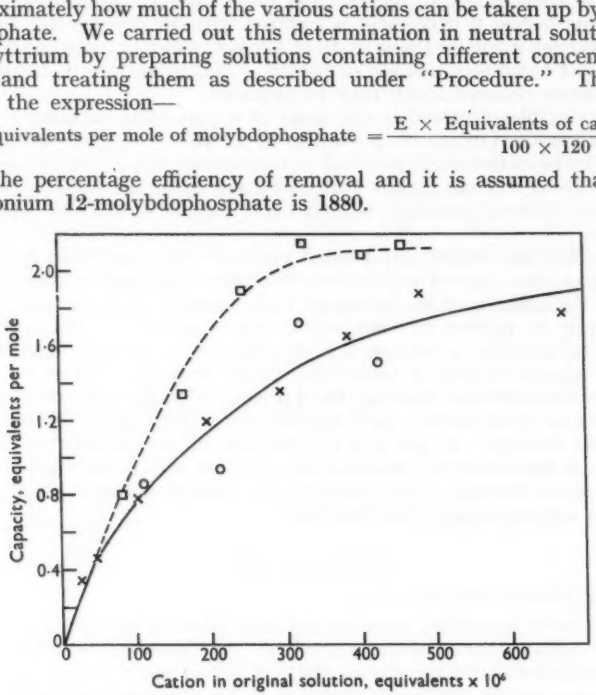

Fig. 1. Capacity of ammonium 12-molybdophosphate for strontium, yttrium and caesium: ×, strontium; ○, yttrium; □, caesium

The results are shown graphically in Fig. 1, from which it can be seen that the values increase, as would be expected, with the amount of cation used, a limit being reached when sufficient cation is present to saturate the material in one passage. It is interesting to note that the limiting value is attained earlier for caesium than for strontium or yttrium, which appear to follow approximately the same curve. Perhaps this is another indication of the greater readiness with which caesium is taken up by the molybdophosphate.

The capacity for caesium was also determined by pouring solutions containing the same amount of labelled caesium in different volumes through ammonium 12-molybdophosphate;

the values obtained were independent of the volumes of solutions used. The amount of caesium stated by Buchwald and Thistlethwaite[2] to be removed from solution is rather less than the saturation value shown in Fig. 1; this is to be expected since these workers used equilibrium rather than saturation conditions.

For the assay of trace amounts of radioactive caesium, strontium or yttrium, the important points are that more than 1 mg of cation is removed almost quantitatively from neutral solution merely by pouring the solution through a small filter-paper supporting 120 mg of ammonium 12-molybdophosphate and that the efficiency of the process, for caesium at least, appears to be independent of the volume of solution containing the cation. The capacity of 120 mg of molybdophosphate for caesium appears to be more than adequate for the quantitative removal of caesium-137 from samples of rain or natural water handled in an assay, provided that a large excess of thallous ions is absent. For other nuclides, such as strontium-90, interfering cations must not be present in significant amounts.

ASSAY OF RADIOACTIVITY—

Fission-product cations other than caesium are readily and quantitatively removed from ammonium 12-molybdophosphate by washing with a little dilute nitric acid. There is therefore little difficulty in preparing a source of these cations for counting; the dilute nitric acid solution can be counted in a liquid counter of the type described by Veall[5] or can be evaporated to provide what is essentially a weightless source for end-window counting. It is, however, difficult to elute caesium-137, except by using a large volume of dilute nitric acid containing thallous or caesium ions, and the procedure originally adopted was to dissolve the molybdophosphate in a little dilute ammonia solution. A liquid Geiger counter is relatively inefficient for detecting and measuring low-energy beta-particles, such as are emitted by caesium-137, and evaporation yields a source for end-window counting that is far from weightless and hence requires considerable correction for self-absorption if assayed via its beta-particles. The preparation of an essentially weightless source has been described in unpublished work by M. J. Hiller, who passed the ammoniacal solution of molybdophosphate through a small column of Zeo-Karb 225, washed out most of the solids (but not caesium) with dilute ammonia, eluted caesium with dilute hydrochloric acid, evaporated the solution, and removed ammonium salts by volatilisation.

A much simpler procedure was satisfactory when the technique of slowly pouring solutions through a small filter-paper supporting ammonium 12-molybdophosphate had been adopted. This consisted in drying the filter by suction, carefully removing the filter-paper from the funnel, without disturbing the molybdophosphate, and counting it under an end-window Geiger counter. The interesting point is that, for microgram amounts of caesium, no correction for self-absorption appeared to be necessary, the same amount of caesium-137 giving approximately the same counting rate when absorbed by molybdophosphate as when prepared as a weightless source. Either the small amount of caesium is absorbed entirely at the surface of the bed of molybdophosphate or back-scatter from the molybdenum atoms in the precipitate compensates for self-absorption. Self-absorption is also negligible for strontium-89; this is not surprising, since beta-particles from this source are more energetic than those from caesium-137.

The samples of ammonium 12-molybdophosphate containing caesium-137 were counted with an end-window Geiger tube and also, in order to avoid corrections for absorption, with a gamma-scintillation counter. The former method was preferred because of its greater simplicity, greater over-all efficiency and lower background (even when a single-channel pulse analyser was used with the scintillation counter).

CORRECTION FOR SELF-ABSORPTION WITH MOLYBDOPHOSPHATE SOURCE—

One-millilitre portions of solutions containing trace amounts of caesium-137 or strontium-89 were carefully evaporated to dryness on an aluminium planchet, and the residues were counted with a Mullard end-window Geiger counter, type MX123. Further 1-ml portions were allowed to flow through 120 mg of ammonium 12-molybdophosphate supported on filter-paper in a 1-inch diameter de-mountable Buchner funnel. The filtrates were checked for radioactivity to ensure that removal of the radioactive cations had been complete. The filter-papers were removed from the funnels, care being taken not to disturb the molybdophosphate, dried under an infra-red lamp and counted in the same position under the same counter as the "weightless" samples. The two counting rates were then compared, and no significant difference was found for either nuclide.

METHOD

PROCEDURE—

Ammonium 12-molybdophosphate was prepared by adding 1 ml of concentrated nitric acid and 0·5 g of ammonium nitrate in approximately 7 ml of distilled water to a solution containing 6 mg of phosphate ion, as ammonium dihydrogen orthophosphate. A 3-ml portion of 10 per cent. ammonium molybdate solution was then added, and the mixture was placed in a water bath at 80° C for 20 minutes. The precipitate was separated, under slightly reduced pressure, on a Whatman No. 1 filter-paper in a 1-inch diameter de-mountable Buchner funnel and washed with distilled water until all excess of acid had been removed. Care was taken to ensure that the ammonium 12-molybdophosphate (approximately 120 mg) was distributed evenly over the filter-paper.

Ten-millilitre portions of the labelled solutions were counted in a liquid counter and then slowly poured through the molybdophosphate. Suction was applied, and a flow rate of approximately 2 ml per minute was usually achieved. The filters were washed, each combined filtrate and washings was concentrated by evaporation, and its volume was adjusted to 10 ml in a calibrated flask. These solutions were then counted. After all counting rates had been corrected for lost counts and background, the efficiency of removal of the labelled cation from solution was calculated from the expression—

$$\text{Efficiency of removal, \%} = \frac{100\,(A - B)}{A},$$

where A is the count rate of the original solution and B is the count rate of the combined filtrate and washings.

For scandium-46, the beta-radiation from which ($E_{max.} = 0{\cdot}36$ MeV) is too weak to be counted efficiently with a liquid counter of the type used, the required activities were precipitated from solution on yttrium fluoride, as carrier, and the precipitates were counted with a gamma-scintillation counter.

TABLE I

REMOVAL OF MULTIVALENT FISSION-PRODUCT CATIONS FROM SOLUTION

Each sample consisted of 10 ml of solution at pH approximately 7 containing a trace concentration of nuclide

Nuclide present	Corrected activity of original solution (A), counts per minute	Corrected activity of filtrate (B), counts per minute	Cation removed from solution,* %
Strontium-89	1262	29	98
Yttrium-91	2769	5	100
Yttrium-91†	2511	1995	20
Cerium-144/praseodymium-144 ..	3422	42	99
Barium-140/lanthanum-140	7703	6	100
Scandium-46	2679	10	100

* Calculated from the expression $\frac{100\,(A - B)}{A}$.

† One millilitre of saturated solution of EDTA added.

TABLE II

EFFECT OF THALLOUS IONS ON REMOVAL OF CAESIUM FROM SOLUTION

Each sample consisted of 10 ml of solution containing 0·55 μg of Cs^+ labelled with caesium-137

Amount of thallous ion present, mg	Corrected activity of original solution (A), counts per minute	Corrected activity of filtrate (B), counts per minute	Caesium removed from solution,* %
0·001	1012	7·6	99·3
9·3	1393	7·1	99·5
18·5	1763	517	70·7
174	1352	956	29·3

* Calculated from the expression $\frac{100\,(A - B)}{A}$.

RESULTS

The proposed method was applied to solutions containing trace amounts of various nuclides in order to study the efficiency of removal of multivalent cations from solution; the results are shown in Table I and Figs. 2 and 3. The effect of thallous ions on the removal of caesium from solution was also studied, and the results are shown in Table II.

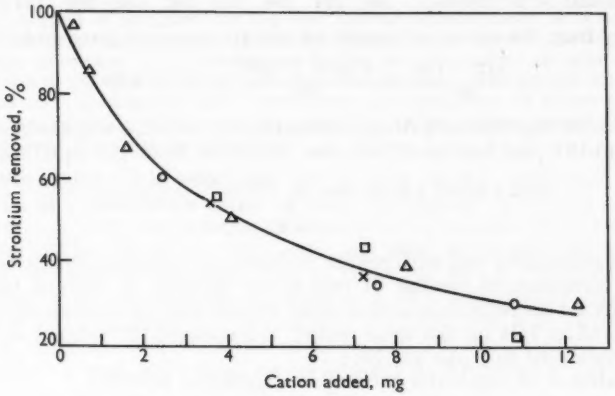

Fig. 2. Removal of strontium-89 from solution: ×, calcium ions added; □, calcium ions and EDTA added; ○, magnesium ions added; △, strontium ions added

APPLICATION OF THE METHOD

DETERMINATION OF CAESIUM-137 IN RAIN WATER—

Owing to lack of rain, the collection of an adequate sample of rain water for the assay of caesium-137 has recently been difficult, and the only sample available (about 4 litres, collected during the late autumn of 1958 at Oadby, Leicestershire) had been previously

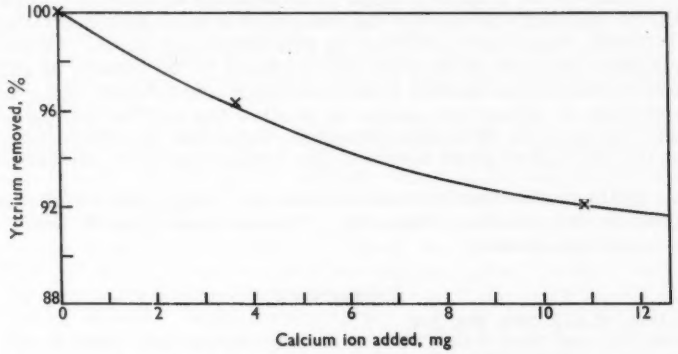

Fig. 3. Removal of yttrium-91 from solution

treated with barium chloride and sodium carbonate. This sample had been collected and treated in polythene vessels and had never been in contact with glassware. A 1100-ml portion of the sample was acidified with dilute nitric acid and allowed to pass through 120 mg of ammonium 12-molybdophosphate as described. After the filter had been dried by suction, the filter-paper and molybdophosphate were mounted on an aluminium planchet and counted in shelf No. 1 of a square lead castle (ERD pattern) under a Mullard end-window Geiger counter, type MX123.

Owing to the low activity of the final sample of ammonium 12-molybdophosphate, count rates for sample *plus* background and for background were recorded alternately until eight readings for each had been obtained. Each count was timed by an automatic timer and was of 20 minutes' duration; the results were—

Sample *plus* background, counts per 20 minutes	297,	319,	330,	334,	294,	321,	314,	327 (Mean 317 ± 13·8)
Background, counts per 20 minutes ..	190,	224,	196,	217,	192,	182,	200,	192 (Mean 199 ± 13·4)

The activity from the source, as counts per minute, was calculated from the expression—

$$\frac{317 - 199}{20} \pm \frac{\sqrt{13{\cdot}8^2 + 13{\cdot}4^2}}{20} = 5{\cdot}9 \pm 0{\cdot}96.$$

An over-all counting efficiency of approximately 20 per cent. was assumed, and the total activity (caesium-137 *plus* barium-137*m*) was calculated from the equation—

$$\text{Total activity, } \mu\mu\text{c per litre} = \frac{(5{\cdot}9 \pm 0{\cdot}96) \times 5 \times 1000 \times 10^{12}}{1100 \times 3{\cdot}7 \times 10^{10} \times 60}$$
$$= 12 \pm 2.$$

This value agrees fairly well with results obtained for samples collected up to the middle of 1958.[6] The strontium-90 content of rain water sampled at Milford Haven is quoted as 6·7 $\mu\mu$c per litre for the second quarter of 1958,[6] and the ratio of caesium-137 to strontium-90 deposited is quoted as 1·34 for the same period; the caesium-137 content of this rain water was therefore equivalent to 9 $\mu\mu$c per litre.

Similar treatment of tap-water yielded no significant activity.

Conclusions

Microgram amounts of many cations, including those of the important fission products caesium-137/barium-137*m*, strontium-90/yttrium-90 and cerium-144/praseodymium-144, are efficiently removed from neutral solution by passage through a pre-formed precipitate of ammonium 12-molybdophosphate supported on filter-paper in a de-mountable Buchner funnel. Only caesium is retained when the precipitate is washed with dilute nitric acid, and any long-lived fission-product activity remaining under these conditions is probably due to caesium-137.

If present in sufficient amounts, calcium and magnesium interfere with the assay of strontium-90/yttrium-90 by a method based on ammonium 12-molybdophosphate, and the presence of EDTA offers little advantage, the removal of yttrium from neutral solution being, as might be expected, considerably inhibited by this complexing agent. On the other hand, only relatively large amounts of thallous ions (unlikely to be present in natural waters) appear to affect the removal of caesium from dilute nitric acid solution, and a simple method for the determination of radioactive caesium is to allow the acidified sample to flow slowly through a bed of ammonium 12-molybdophosphate supported on a filter-paper, to dry the precipitate by suction, and to count with a Geiger counter having a thin end-window.

One of us (S.D.) thanks the International Atomic Energy Agency for supporting the research programme and granting a fellowship. We also thank Miss M. Gibbs, who carried out much of the routine counting.

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The Determination of Traces of Lead in Telluric Acid

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A method is described for the colorimetric determination of concentrations greater than 0·1 p.p.m. of lead in telluric acid. Lead is concentrated into not more than 0·5 g of tellurium by reducing a solution of telluric acid at pH 1·6 to 2·3 with a suitable amount of hydrazine. The normal dithizone method for the isolation and colorimetric determination of traces of lead is not applicable in presence of sexavalent tellurium, but up to 0·5 g of the quadrivalent form can be tolerated.

Lead is a common impurity in tellurium, and in work on the purification of this element it became necessary to determine traces of lead, particularly in telluric acid. The usual methods for separating lead from other materials depend on an extraction procedure involving the use of diethyldithiocarbamate or dithizone, and dithizone is also the most satisfactory reagent for the colorimetric determination of traces of lead.[1] Preliminary experiments indicated that diethyldithiocarbamate cannot be used, as it is extensively oxidised by telluric acid. The latter also suppresses the formation of lead dithizonate in strongly ammoniacal solution, so that, when the double-extraction procedure first described by Snyder[2] and later modified by Sandell[1] is used, recovery of lead is incomplete in presence of 0·5 g of telluric acid.

Experimental

Effect of quadrivalent tellurium on isolation and determination of lead with dithizone—

Tellurium (obtained from J. Lowenstein Co. Ltd.) having a purity of 99·9999 per cent. was dissolved in diluted nitric acid (1 + 1) to give a solution of quadrivalent tellurium. An 8·3-μg portion of lead, as nitrate, was added to each of different amounts of this solution, and the lead in the samples was isolated and determined as described by Sandell[1]; the results were—

Tellurium present, g	..	0·0	0·002	0·012	0·06	0·23	0·57
Lead found, μg	.. ..	8·2	8·2	8·1	8·3	8·2	8·3

The presence of up to 0·5 g of quadrivalent tellurium, therefore, has no effect on the determination of traces of lead by this method. The citrate reagent used during the extraction with dithizone forms a complex with quadrivalent tellurium, which, under the alkaline conditions used, is precipitated if more than 0·5 g of tellurium is present. When this occurs the recovery of lead is low.

Quadrivalent tellurium appears to react with dithizone under the conditions of this extraction procedure. The final carbon tetrachloride solution in which the colour of the lead dithizonate is measured becomes increasingly yellow as the amount of tellurium present in the original solution increases. This colour cannot be produced by any oxidation products of dithizone formed during the preliminary extraction, as such products would hardly be extracted by dilute nitric acid (1 + 100) and should not therefore appear in the final determination. This yellow colour does not interfere with the determination of lead; at the wavelength used for measuring the dithizone colour (520 mμ) it has a low absorption, equivalent to less than 0·1 μg of lead. Maximum absorption occurs at 425 to 430 mμ, and Mabuchi,[3] who used widely different conditions, found that quadrivalent tellurium and dithizone formed a complex having a maximum at 430 mμ. When only sexavalent tellurium is present, no yellow colour is formed.

Recovery of lead from solutions of telluric acid—

A few preliminary experiments were carried out without control of the pH. An excess of hydrazine hydrate solution was added to a solution of 0·5 g of telluric acid containing added lead, and all the tellurium was precipitated; analysis of the precipitate showed that it contained most of the added lead. However, it is usually necessary to take a weight of telluric acid considerably greater than 0·5 g in order to have present an amount of lead suitable for determination, and the lead must be concentrated into not more than 0·5 g of tellurium.

This may be accomplished by using only enough hydrazine to precipitate a small proportion of the tellurium; all the lead is co-precipitated.

In a series of recovery experiments, 25·0-μg portions of lead were added to separate solutions containing 1·5 g of purified telluric acid, and tellurium was precipitated by 2 ml of a 10 per cent. solution of hydrazine hydrate (purified as described under "Reagents") from solutions at different pH values. The results were—

Original pH	1·10	1·20	1·30	1·44	1·60	1·75	1·90	2·05	2·20	2·30
pH after precipitation	1·42	1·61	1·68	1·82	2·04	2·16	2·25	2·34	2·49	2·63
Lead found, μg	19·2	24·9	25·4	25·1	25·6	24·7	25·3	24·7	24·0	23·9

The change in pH caused by adding 2 ml of purified hydrazine hydrate solution (pH 9), subsequently precipitating and boiling is governed by the extent to which the solution is buffered. In the experiments mentioned above, the increase was 0·3 to 0·4 unit of pH, whereas when 15 g of telluric acid were present in the sample solution and 2 ml of hydrazine hydrate solution were used, the increase was only 0·05 unit of pH. For a solution containing 15 g of purified telluric acid at pH 1·20, the final pH was 1·25, and the recovery of 8·3 μg of added lead was only 1·5 μg. Since at this initial pH recovery of added lead was complete in presence of 1·5 g of telluric acid, the pH after precipitation is the controlling factor. The results above show that recovery of added lead is complete in the pH range 1·6 to 2·35; at lower pH values precipitation of lead is incomplete, and at higher pH values there is difficulty because the amount of tellurium precipitated increases to more than the tolerable limit (0·5 g).

COMPLETENESS OF PRECIPITATION OF LEAD WITH A SMALL PROPORTION OF TELLURIUM—

To check the completeness of precipitation of lead by the method described above, attempts were made to determine the amount of lead remaining in solution. Since most of the lead is precipitated, the bulk of any lead remaining in solution should be precipitated when a further small proportion of the tellurium present is reduced to the element. Lead was therefore determined in second precipitates. This was done in presence of up to 15 g of telluric acid, and up to 25 μg of lead were added; the largest amount of lead found was 0·2 μg, and the reagent blank value was 0·7 μg of lead. Within these limits the recovery of lead in one precipitation was complete.

EFFECT OF CHLORIDE, SULPHATE AND CITRATE ON RECOVERY OF LEAD—

The presence in telluric acid of other cations as impurities would not be expected to interfere, as, if these ions were also precipitated when the telluric acid was reduced, they would be separated during the isolation of lead. However, the formation of lead - anion complexes might prevent co-precipitation of lead. Nitrate was without effect, as lead was added in nitric acid solution, but the effects of three other common anions, chloride, sulphate and citrate, were examined. Portions of lead (25 μg) were added to separate solutions each containing 1·5 g of purified telluric acid and one of these anions, and lead was recovered by the proposed procedure. The final pH of each solution was between 1·92 and 2·06; the results were—

Foreign anion	Chloride	Sulphate	Citrate
Concentration of anion, *M* ..	0·3	0·25	0·1
Lead found, μg	25·9	25·1	0·0

These results show that, although chloride and sulphate ions are without effect, citrate ions, even in lower concentrations, prevent co-precipitation of lead with tellurium.

METHOD

REAGENTS—

The hydrochloric and nitric acids and ammonia solution used were obtained from the British Drug Houses Ltd. ("Lead-free for Foodstuffs Analysis").

Telluric acid—Remove lead from analytical-reagent grade telluric acid by passage through a column of Amberlite IR-120 in the hydrogen form at pH 4.

Hydrochloric acid, dilute (1 + 9).

Ammonia solution, diluted (1 + 1).

Nitric acid, concentrated and dilute (1 + 100).

Hydrazine hydrate solution—Adjust the pH of a 10 per cent. v/v aqueous solution of laboratory-reagent grade hydrazine hydrate to 9 with hydrochloric acid, and remove lead

by shaking with successive portions of dithizone solution in carbon tetrachloride until there is no colour change. Remove excess of dithizone by shaking with successive portions of chloroform until colourless. (Hydrazine hydrate is more convenient to use than is the hydrochloride, as less adjustment of the pH is involved.)

Hydroxylamine hydrochloride solution—Prepare and purify as described by Sandell.[1]

Potassium cyanide solution—Prepare and purify as described by Sandell.[1]

Ammonia - cyanide - sulphite solution—Prepare and purify as described by Sandell.[1]

Dithizone solution—Prepare and purify as described by Sandell.[1]

Ammonium citrate solution—Adjust the pH of a solution containing 200 g of analytical-reagent grade citric acid in 250 ml of water to 9 by adding analytical-reagent grade ammonia solution, and cool the solution in ice as required. Dilute the final solution to 500 ml, and remove lead as described by Sandell.[1]

Carbon tetrachloride—Analytical-reagent grade.

Standard lead solution—Dissolve 0·1667 g of dried analytical-reagent grade lead nitrate in 250 ml of dilute nitric acid (1 + 100), and dilute 5 ml of the solution to 500 ml with that acid. This gives a solution containing 4·17 μg of lead per ml.

PREPARATION OF STANDARD GRAPH FOR LEAD—

Take 0, 0·5, 1·0, 1·5, 2·0 and 2·5-ml portions of standard lead solution, dilute each to 10·0 ml with dilute nitric acid (1 + 100), and carry out the extraction procedure described by Sandell[1] for isolating lead (see Note), with two exceptions. Instead of indicator solution, it is more convenient to use a pH meter; the capacity of 4-cm spectrophotometer cells necessitates an increase to 25 ml of the volume of organic phase in the subsequent determination, so an increase in the volume of the aqueous phase is desirable; this is done by increasing to 10 ml each of the portions of dilute nitric acid (1 + 100) used to secure reversion of lead to the aqueous phase.

To the combined nitric acid solutions add 20 ml of ammonia - cyanide - sulphite solution and 25 ml of dithizone solution. Shake for 1 minute, allow the layers to separate, filter the carbon tetrachloride layer through a plug of filter-paper, and measure its optical density in 4-cm cells at 520 mμ with a Unicam SP600 spectrophotometer. Use the solution containing no added lead as reference.

For 1-cm spectrophotometer cells, take 0, 1·0, 2·0, 4·0, 6·0 and 7·0-ml portions of standard lead solution, and continue as described above; in this way the range 0 to 30 μg of lead is covered. The maximum deviations of the graphs from linearity represented 0·2 and 0·9 μg of lead for 4- and 1-cm cells, respectively.

NOTE—The procedure described by Sandell[1] differs considerably from that found in earlier editions of the book.

PROCEDURE—

Dissolve a suitable weight of telluric acid (up to 15 g) in 50 to 250 ml of water, and add hydrochloric acid to adjust the pH to a value between 1·6 for 1·5 g of sample and 2·0 for 15 g. Add 1·5 to 2·0 ml of hydrazine hydrate solution, heat just to boiling-point, and set aside for at least 3 hours. Measure the pH of the cold supernatant liquid, which should be in the range 1·6 to 2·1. Draw the supernatant liquid through a sintered immersion filter (porosity No. 2), wash the precipitate three times with water, and remove the washings. Dissolve the precipitate in 5 ml of concentrated nitric acid, boil to expel oxides of nitrogen, and isolate and determine lead as described for the standard graph. Use as reference a reagent blank solution prepared by treating 5 ml of concentrated nitric acid as described above.

RESULTS

The recovery of lead added to solutions of purified telluric acid is shown in Table I; it can be seen that recovery is complete over a wide range of conditions.

It is not possible to measure the complete reagent blank value, but only that portion of it subsequent to the precipitation. The reagent blank value as measured is in the range 0·7 to 1·2 μg of lead. The only reagents not covered by this value are a few drops of hydrochloric acid (containing not more than 0·005 p.p.m. of lead) and 2 ml of a 10 per cent. solution

TABLE I

RECOVERY OF ADDED LEAD FROM SOLUTIONS OF PURIFIED TELLURIC ACID

Lead added, μg	Lead found in solution containing— 1·5 g of telluric acid, μg	15 g of telluric acid, μg
Optical density measured in 1-cm cells—		
0·0	0·1	0·4
4·2	4·1	5·3
8·3	8·4	9·1
16·7	16·6	16·8
25·0	25·1	25·2
29·2	29·6	29·8
Optical density measured in 4-cm cells—		
0·0	0·1	0·3
1·1	0·9	1·4
2·1	2·2	2·4
4·2	4·3	4·2
6·3	6·2	6·4
8·3	8·3	—
10·5	—	11·0

of hydrazine hydrate, which has itself been purified. The total amount of lead in these reagents must be exceedingly small, so that the measured blank value may be considered to be the true value.

There appears to be no reason why weights of telluric acid greater than 15 g should not be used as sample. The lower limit for determining lead would then be below the 0·1 p.p.m. claimed for the proposed method.

The work described was carried out as part of the research programme of the National Chemical Laboratory, and this paper is published by permission of the Director of the Laboratory.

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Notes

OBSERVATIONS ON THE CORRELATION OF ANTICHOLINESTERASE EFFECT WITH SOLANINE CONTENT OF POTATOES

It has recently been noticed in this laboratory and elsewhere[1,2] that potatoes normally contain a water-soluble substance having anticholinesterase activity. We had to examine a sample of imported new potatoes said to have caused poisoning, and the opportunity was taken of examining a view expressed by the Russian worker Pokrovsky. He contended[1] that "solanine anti-cholinesterase activity can be regarded as one of the principal rapid approximate methods for determination of the concentration of toxic glycoalkaloids in potatoes." Incidentally, this statement carries at least a strong implication that the anti-esterase activity of the potato is principally due to solanine, a view with which Orgall, Vaidya and Dahm[2] disagree. These workers in America hold that the properties of the anti-esterase agent permit it to be identified neither as solanine nor as any other of the better known alkaloids of the *Solanaceae*.

Experimental

Anticholinesterase experiments on juice from the tubers were carried out by the micro potentiometric method described by Hensel and his co-workers.[3] Samples were finely shredded, and juice was expressed by pressing in cloth. Solanine was used as a standard inhibitor for reasons of practical convenience and ease of calculation and expression. Dilutions of juice were made as necessary to bring the observed degree of esterase inhibition within the most advantageous range for exact measurements, *i.e.*, 20 to 80 per cent. Dried human blood plasma was used as a source of cholinesterase. Determinations of solanine were made on alcoholic extracts of the comminuted tubers by a well known spectrophotometric method.[4]

Results

The results of our experiments are shown in Table I.

Table I

Solanine contents and anticholinesterase effects of potatoes

Sample No.	Description of sample	Solamine content found by spectrophotometric method,[4] mg per 100 g	Anticholinesterase effect of juice (as equivalent amount of solanine), mg per 100 g
1	From Eastern Mediterranean country; suspected of causing symptoms of poisoning	45	84
2	Locally purchased old	1	2
3	Sprouted and green old	8	6
4	Sample No. 3 after a further month's storage ..	36	26
5	New, said to be *ex* Canary Islands	6	18
6	New, said to be *ex* North Africa	3	8

The absence of any chloroform-soluble anti-esterase activity indicated that organo-phosphorus insecticide residues were not present in the samples.

Comparison of the results by the two methods on new potatoes having high contents of solanine suggests one of two explanations for the differences: (*i*) that an anti-esterase other than solanine is present, as suggested by Orgall, Vaidya and Dahm[2] and (*ii*) that Baker, Lampitt and Meredith's method may give results considerably lower than the true values in certain circumstances.

It would be a matter of considerable difficulty to decide with certainty between these hypotheses. An experiment with more limited aims was devised, the techniques immediately at our disposal being used. In effect, the anticholinesterase method was used to monitor the extraction stages of Baker, Lampitt and Meredith's method.

It was found that about 20 per cent. of the anticholinesterase activity of new potatoes having high contents of solanine was not removed by extraction with ethanol for 16 hours in a Soxhlet apparatus and could be recovered by steeping the residue in water overnight. The filtrate from which the solid solanine had been precipitated at pH 9·4 was found to contain about 7 per cent. of the total anticholinesterase activity of the potato. The solid "solanine" isolated by precipitation

with ammonia solution at pH 9·4 was found to have an anticholinesterase activity corresponding to about twice the amount of solanine found in it by the spectrophotometric method.[4]

Discussion of results

The anticholinesterase effect of potato juice appears to have an approximate direct relationship to the solanine content of the potato as determined by the spectrophotometric method. Our experience with potatoes known to be poisonous to humans has been limited to one sample, and clearly no general theory or conclusions can be based on it. We have, however, thought it proper to publish these observations in view of the obvious rarity of occasions when suitable materials and techniques are available for making and comparing the three types of observation, *i.e.*, toxicity, solanine content and anticholinesterase activity. None of the methods is specific for solanine, and the results cannot therefore prove or disprove Pokrovsky's implied contention that the anti-esterase effect of the potato is principally due to solanine. However, the results indicate that, contrary to the findings of Orgall, Vaidya and Dahm, over 90 per cent. of the total anti-esterase activity is precipitated at pH 9·4.

Permission to publish this Note has been given by the Department of Scientific and Industrial Research. We thank the Director of the Public Health Laboratory Service for providing the material that led to this investigation.

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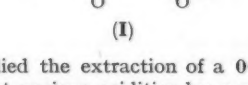
RAPID EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH 2-THENOYLTRIFLUOROACETONE

The chelating agent 2-thenoyltrifluoroacetone (**I**), commonly known as TTA, has found wide application in the separations of actinide metals. Several workers have reported extraction of



(**I**)

uranyl ion by TTA.[1 to 5] King[2] studied the extraction of a 0·1 *M* solution of uranium^{IV} from lithium perchlorate - perchloric acid at various acidities by a solution of TTA (0·17 to 1·53 *M*) in benzene. Hyde[1] extracted trace concentrations of uranyl nitrate from dilute nitric acid solution with a 0·2 *M* solution of TTA in benzene; he observed quantitative extraction at pH 3·0. Neptunium^{IV}, plutonium^{VI} and zirconium^{IV} have been separated from uranium^{VI} by extraction with TTA at relatively high acidities. By careful control of pH, thorium^{IV} can be separated from uranium^{VI}.

In the proposed method, the yellow colour of the uranyl - TTA complex in benzene has been exploited for the rapid spectrophotometric determination of milligram amounts of uranium^{VI}. The optimum conditions have been carefully selected from a critical study of the various factors involved in extracting, separating and determining milligram amounts of uranium. A preliminary report of this work has been published.[6]

Method

Apparatus—

Optical-density measurements were made with a Hilger quartz spectrophotometer and 1-cm quartz cells; pH values were measured with a Cambridge pH meter.

Reagents—

All the chemicals used were, unless otherwise stated, chemically pure or of analytical-reagent grade.

Approximately 0·15 *M* solutions of 2-thenoyltrifluoroacetone, melting-point 42° to 43° C (obtained from L. Light & Co.), in benzene were used. With more dilute solutions (about 0·01 *M*), extraction was found to be extremely slow.

A stock solution of uranyl nitrate, prepared by dissolving 2·1 g of the salt (obtained from Mallinckrodt) in 1 litre of 1 per cent. nitric acid, was standardised gravimetrically by the oxine method. One millilitre of the solution contained 0·85 mg of uranium. For extraction and spectrophotometric studies the stock solution was diluted 1 + 4. so that the uranium content was 0·17 mg per ml.

A buffer solution of pH 6·0 was prepared by dissolving 77 g of ammonium acetate in water, acidifying with acetic acid to pH 6·0, and diluting to 1 litre.

General procedure—

A suitable aliquot (5 ml) of diluted uranyl nitrate solution was mixed with 10 ml of buffer solution of pH 6·0 and then diluted to 25 ml with water. For pH studies the buffer solution was omitted except when a pH of about 6·0 was required; the pH of the uranyl solution was brought to the required value by adding 0·01 *N* hydrochloric acid or 0·01 *N* sodium hydroxide, and the solution was then diluted to 25 ml with water. For studies of the effects of other ions, the solution containing the ion was added before the buffer solution. The aqueous solution thus prepared was introduced into a 250-ml separating funnel and shaken for 10 minutes with 10 ml of a 0·15 *M* solution of TTA in benzene. The aqueous layer was transferred to a beaker, and the benzene layer was withdrawn into a 25-ml calibrated flask. The aqueous layer was rinsed with 5 ml of benzene in the separating funnel, and the benzene layer was withdrawn as before into the calibrated flask. The combined yellow benzene extracts were finally diluted to 25 ml with benzene, and the optical density was measured at 430 mμ against a reagent blank solution. The corresponding uranium concentration was read from the calibration graph described below.

The aqueous layer, after extraction, was used for pH measurements.

Results and discussion of the method

Absorption spectrum—

The spectrum of the yellow uranyl - TTA solution has an absorption maximum at 410 mμ; the optical density becomes practically negligible above 500 mμ. The colourless blank solution, however, exhibits appreciable absorption around 410 mμ, which sharply decreases and becomes insignificant from 430 mμ onwards. All optical-density measurements were therefore made at 430 mμ. The molar extinction coefficient at 430 mμ is 1954 $\pm$ 40 (calculated on the basis of uranium).

Effect of pH—

The extraction of uranium^{VI} by a solution of TTA in benzene was studied over the pH range 0·5 to 8·0. The distribution ratios, D, were calculated[7] from the extraction curve from the relationship—

$$1 - \frac{\text{Extraction, \%}}{100} = \frac{V}{D\,V' + V}$$

where V and V' refer to the volumes of the aqueous and organic phases, respectively (see Table I).

The extraction starts after pH 1·2. At pH 3·0 the extraction is 97 per cent. (D = 80·8) and

Table I

Distribution ratios of uranyl thenoyltrifluoroacetonate between benzene and aqueous solution as function of pH

pH	Uranium extracted into benzene, %	D
1·0	0·0	—
1·3	2·00	0·05
1·5	7·00	0·19
1·7	12·00	0·34
2·0	29·00	1·02
2·3	62·00	4·08
2·5	78·00	8·86
2·7	88·00	18·35
3·0	97·00	80·83
3·5	100	—
7·0	100	—

from pH 3·5 onwards quantitative extraction (100 per cent.) is observed. The pH region 3·5 to 8·0 can safely be used for 100 per cent. extraction of uranium by TTA. This is in excellent agreement with the observation of Hyde,[1] who worked on traces of uranium and noted quantitative extraction at pH >3·0.

CALIBRATION GRAPH—

To study the adherence of the coloured solution to Beer's law, a calibration graph for the uranyl complex was constructed by measuring optical densities at 420 and 430 mμ against a reagent blank solution at pH 5·4. The graphs were linear at both wavelengths, which indicated that the uranyl - TTA system obeyed Beer's law. However, 430 mμ was preferable, since its use permitted determinations over a wider concentration range; the optimum range is from 5 to 50 mg of uranium per litre.

CONCENTRATION OF REAGENT—

The concentration of TTA was varied from 0·008 to 0·15 *M*, other factors being kept constant. The uranium concentration was maintained constant in these tests. The results of these tests indicated that the optimum concentration of reagent is 0·15 *M*. Ten millilitres of 0·15 *M* TTA are adequate for colour development—essentially the same optical density (0·280) is obtained even with 20 ml of reagent solution. With dilute solutions (0·015 or 0·008 *M*) there is little or no extraction.

STABILITY OF COLOUR—

The optical density of a solution of uranyl - TTA complex, prepared as described under "General Procedure," was measured after 15 minutes, 30 minutes, 1, 24, 48, 72, 96 and 168 hours. The results showed that the colour was stable up to 96 hours, after which decomposition occurred; after 168 hours the optical density had decreased by about 9 per cent.

SALTING-OUT AGENTS—

Several salting-out agents—sodium, magnesium, barium and aluminium nitrates—were examined in order to observe their effect on the extraction of uranium by TTA. Sodium nitrate exhibited a salting-out effect by enhancing the extraction. Barium nitrate did not appear to have any effect, whereas magnesium nitrate interfered and aluminium nitrate gave a colour reaction.

EFFECTS OF THE PRESENCE OF OTHER IONS—

The ions listed below (100 mg of each, except as otherwise stated) were carried through the proposed procedure—

Ag^+, Cu^{2+}, Pb^{2+}, Hg^{2+}, Fe^{3+}, Ba^{2+}, Zr^{4+}, Th^{4+}, CO_3^{2-}, $C_2O_4^{2-}$, citric acid and tartaric acid.

The results are shown in Table II. Among the cations tried, silver, thorium and zirconium interfere; copper and iron interfere by forming colours. Oxalate and carbonate, among the anions, seriously interfere. Citrate and larger amounts of tartrate also interfere. The uranyl - TTA system obviously can tolerate 100-mg amounts of cations such as lead^{II}, mercury^{II} and

TABLE II

EFFECTS OF VARIOUS IONS

Amount of uranium present in each test, 0·85 mg

Ion	Added as	Amount of ion added, mg	Optical density at 430 mμ
None	—	—	0·279 ± 0·006
Ag^+	$AgNO_3$	100	0·304
Cu^{2+}	$CuSO_4.5H_2O$	100	Colour reaction
Pb^{2+}	$Pb(NO_3)_2$	100	0·275
Hg^{2+}	$HgCl_2$	100	0·284
Fe^{3+}	$FeCl_3.6H_2O$	100	Colour reaction
Ba^{2+}	$BaCl_2$	100	0·276
Zr^{4+}	$ZrOCl_2.8H_2O$	10	0·324
Th^{4+}	$Th(NO_3)_4$	10	0·244
Tartrate*	Tartaric acid	500	0·168
Tartrate*	Tartaric acid	100	0·284
Citrate*	Citric acid	100	0·208
Oxalate*	Oxalic acid	100	0·048
Carbonate*	$Na_2CO_3.10H_2O$	100	0·056

*The pH of the solution containing uranyl nitrate and added ion was adjusted to 6·0 with hydrochloric acid or sodium hydroxide solution, and then the solution was extracted according to the general procedure.

barium. The interfering cations, *e.g.*, silver, thorium, zirconium, copper and iron, can, however, be removed by addition of EDTA (disodium ethylenediaminetetra-acetate) to the aqueous phase before extraction. Thus the selectivity of the proposed method can be greatly enhanced.

Recommended procedure and precision of method

Place in a separating funnel an aqueous solution containing 0·2 to 1·2 mg of uranium, add 10 ml of buffer solution of pH 6·0 (add 2 ml of 0·1 *M* EDTA solution if other cations are present in the original solution), and extract for 10 minutes with 10 ml of a 0·15 *M* solution of TTA in benzene. Measure the optical densities as described under "General Procedure," p. 377. The reagent blank solution should be treated similarly.

From six tests by the recommended procedure with 0·85 mg of uranium the optical density of a solution was 0·279 ± 0·006; the coefficient of variation was ±2 per cent. This indicates that the recommended procedure gives fairly reproducible results. The elegance of the method is that it permits extraction and spectrophotometric determination in one operation taking only 15 to 20 minutes and that it can be rendered selective by adding EDTA as a masking agent. As little as 2 μg of uranium per ml can be detected by the method.

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THE COMPLEXOMETRIC DETERMINATION OF MOLYBDENUM

Lassner and Scharf[1] recently reported the determination of 5 to 30 mg of molybdenum^{VI} by a method involving reduction in sulphuric acid solution to molybdenum^{V} by hydrazine sulphate in presence of disodium ethylenediaminetetra-acetate (EDTA); the excess of EDTA was titrated against 0·05 *M* cupric sulphate at pH 4, with 1-(2-pyridylazo)-2-naphthol as indicator. This was the first mention of a satisfactory means of determining molybdenum directly by using EDTA, although indirect methods, based on the titration of calcium in calcium molybdate, had been described.[2,3]

Unaware that Lassner and Scharf were working on that problem, I have developed a similar method for determining molybdenum with EDTA by following up Pecsok and Sawyer's statement[4] that molybdenum^{V} and EDTA form in acid solutions a stable complex containing two atoms of molybdenum per molecule of EDTA. The method involves reduction of molybdate in hydrochloric acid solution by hydrazine sulphate[5] to molybdenum^{V}. The molybdenum^{V} - EDTA complex is formed, and the excess of EDTA is titrated against zinc chloride solution at pH approximately 4·2, alizarin complexone[6] being used as indicator. When photometric titration and 0·01 *M* solutions of EDTA and zinc chloride were used, from 1 to 11 mg of molybdenum were satisfactorily determined with a maximum error of ±0·05 mg.

Experimental

An attempt was made to titrate the excess of EDTA over the amount required to react with the molybdenum^{V} formed on reduction by hydrazine sulphate against zinc chloride solution. The titration was carried out at pH 5·3, and xylenol orange was used as indicator, since its colour change is superior to those of most other indicators.[7] However, results were low when amounts between 1 and 10 mg of molybdenum were determined with 0·01 *M* zinc chloride as titrant (about

97 per cent. of the molybdenum present was found). The low results were caused by oxidation of about 3 per cent. of the molybdenum^{V} - EDTA complex at pH 5·3 before the excess of EDTA could be titrated. This oxidation was not brought about by atmospheric oxygen, since identical results were obtained when a solution containing 9·60 mg of molybdenum^{V} prepared by passing a solution of sodium molybdate through a silver reductor[8] was analysed by the above-mentioned complexometric method and by a method involving oxidation to molybdenum^{VI} by ceric sulphate solution.[8] Pecsok and Sawyer have also reported that the molybdenum^{V} - EDTA complex is stable to aerial oxidation below pH 7.

The low results at pH 5·3 seem to be associated with the hydrazine sulphate. When the concentration of this substance in the solution is increased ten-fold, the negative error is also increased (about 95 per cent. of the molybdenum present was found). Hydrazine is known to react with dissolved oxygen in weakly alkaline solutions[9] to produce hydrogen peroxide, and it may be that traces of hydrogen peroxide are formed even at pH 5·3. The hydrogen peroxide would then oxidise the molybdenum^{V} - EDTA complex and so give rise to low results. For this reason it was necessary to carry out the titration with zinc chloride solution at a lower pH. However, it was found that xylenol orange would not give a satisfactory end-point below pH 5·0, and therefore alizarin complexone[6] was used. A titration in a solution buffered at pH 5·3 would probably be satisfactory with xylenol orange as indicator if a reducing agent other than hydrazine sulphate could be found. Sulphur dioxide, hydroxylamine hydrochloride and ascorbic acid were tried as reducing agents, but none gave quantitative reduction of molybdenum^{VI} to molybdenum^{V}.

Method

Apparatus—

An E.E.L. titrator (Evans Electroselenium Ltd.) was used, although most filter photometers and spectrophotometers could be adapted for the photometric titrations.

The calibrated flasks used in preparing the standard solutions and the 10-ml microburette used for the titrations were of NPL grade A; other graduated glassware was of grade B.

Reagents—

All materials should be of analytical-reagent grade. The standard and EDTA solutions should be stored in polythene bottles.

Standard sodium molybdate solution—Prepare a solution containing about 0·25 g (accurately weighed) of sodium molybdate dihydrate per 100 ml; this solution is approximately 0·01 *M*. The solute used had a purity of 100·0 per cent., and its molybdenum content was determined by precipitation as lead molybdate.[10]

Standard zinc chloride solution—Dissolve about 0·65 g (accurately weighed) of zinc shot by heating with dilute hydrochloric acid. Evaporate the solution to the first appearance of solid, dissolve the residue in distilled water, and dilute to exactly 100 ml. Dilute 10 ml of this solution to 100 ml.

EDTA solution—Prepare a solution containing about 0·93 g of disodium ethylenediaminetetra-acetate dihydrate per 250 ml.

Buffer solution—Prepare a solution containing 45·9 g of sodium acetate trihydrate per 100 ml.

Hydrazine sulphate solution, saturated, aqueous.

Indicator solution, 0·5 per cent.—Treat 100 mg of alizarin complexone (obtainable from Hopkin and Williams Ltd.) with 2 drops of concentrated ammonia solution and then 7 to 8 drops of 20 per cent. w/v ammonium acetate solution, and dilute to 20 ml.

Procedure—

Place the molybdate solution (approximately neutral) containing 1 to 11 mg of molybdenum in a 50-ml beaker, and adjust its volume to about 10 ml. By pipette, add 1 ml each of concentrated hydrochloric acid and hydrazine sulphate solution. Heat to 95° C, and maintain at this temperature for 5 minutes. Cool, add 10 ml of EDTA solution, by pipette, and transfer to a 50-ml sample holder for the E.E.L. titrator. Insert the stirring rod, and set the stirrer in motion. By pipette, place 5 ml of buffer solution in the sample holder, and add 5 drops of indicator solution.

With use of an Ilford No. 604 filter, set the galvanometer reading (relative optical density scale) to about 8, and titrate the solution with standard zinc chloride solution added from a 10-ml microburette. When the galvanometer readings cease to decrease (dilution effect), take readings at 0·2-ml intervals until the reading begins to increase. Continue to record readings at more

frequent intervals until a further 2 ml of titrant have been added. Plot a graph of galvanometer readings against volume of titrant added. Extend forward the horizontal base line passing through the lowest galvanometer reading, and extend downwards the line of the steepest part of the curve until it intersects the horizontal base line; the intersection marks the end-point. Typical curves are shown in Fig. 1.

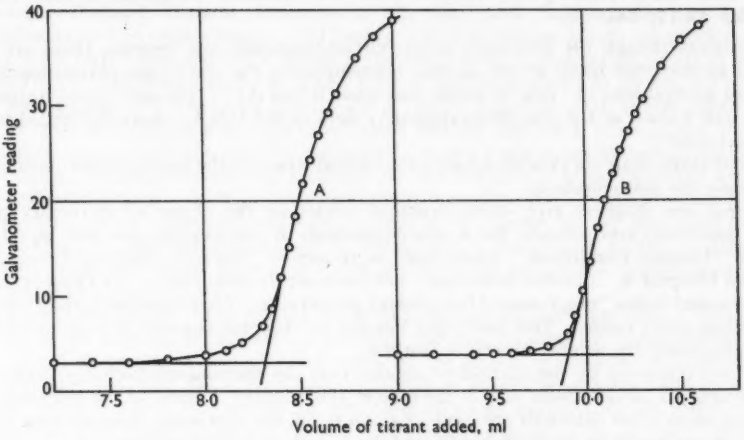

Fig. 1. Titration curves: curve A, 3·21 mg of molybdenum^{V} *plus* 10 ml of EDTA solution (sample) against 0·01050 *M* zinc chloride; curve B, 10 ml of EDTA solution (blank) against 0·01050 *M* zinc chloride

Carry out the same procedure with a blank solution containing no molybdate. (This solution need not be heated to 95° C after the hydrazine sulphate solution has been added.) Subtract the titre for the sample solution from that for the blank solution to obtain the volume of standard zinc chloride solution equivalent to the molybdenum taken.

0·5 ml of 0·01 *M* zinc chloride ≡ 0·9595 mg of molybdenum.

Discussion of the Method

Typical results by the proposed method were—

Molybdenum present, mg ..	1·06	3·21	5·51	7·29	10·65
Molybdenum found, mg ..	1·09	3·20	5·56	7·26	10·61
Error, mg	+0·03	−0·01	+0·05	−0·03	−0·04

The procedure described above can, of course, be used only for pure molybdate solutions or solutions containing only alkali or alkaline-earth metals in addition to molybdate. It will require modification if it is to be used for determining molybdenum in presence of metals other than those just mentioned.

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Book Reviews

PRINCIPLES AND PRACTICE OF GAS CHROMATOGRAPHY. Edited by ROBERT L. PECSOK. Pp. xii + 226. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1959. Price $6.75; 54s.

Voluminous though the literature of gas chromatography has become, there are very few text-books meeting the needs of the analyst contemplating the use of gas chromatography, who has a broad general idea of "how it works and what it can do." The editor and authors of this book—all well known in the gas-chromatography field in the U.S.A.—have succeeded in catering for such a reader.

The first three chapters provide an adequate introduction to the theory of gas chromatography without being too mathematical.

The next ten chapters give sound practical advice on the choice of stationary phase and operating conditions and indicate the available methods of introducing gas and liquid samples. Chapter 6, "Column Conditions," could well be re-named "Factors affecting Efficiency"; this chapter and Chapter 8, "Column Selection," are particularly important. In Chapter 11, several pages are devoted to the "programmed (*i.e.*, rising) temperature" technique for dealing with samples of wide boiling-point range. This technique has not yet become popular in this country, though it is used effectively by several American workers.

There is a tendency by the authors to assume that the thermal-conductivity detector is still almost universal; I do not think such is the case in this country. Some of the information needs modification when other detectors are used—*e.g.*, on p. 52, the maximum temperatures for various stationary phases would be considerably lower for use with an ionisation detector. In Chapter 12, a discussion of the relative merits of different types of detector would have been helpful. I would also have liked to see more space devoted to capillary columns.

The statement on p. 83 that "long columns have increased sample capacity" does not agree with the findings of Cheshire and Scott (*J. Inst. Pet.*, 1958, **44**, 74), who showed that by increasing column length from 4 to 25 feet, the permissible sample load was reduced from 1 to 0·4 mg.

The last chapter gives all the instructions normally needed for the qualitative and quantitative interpretation of chromatograms, even including the difficult instances of unsymmetrical and overlapping peaks.

The text is followed by 69 pages of bibliography consisting of 710 references. Titles of papers are included; this fact makes the bibliography not only the most complete so far, but an excellent guide to an overwhelming mass of literature.

I would recommend this book to any analyst using or about to use gas chromatography.

B. A. ROSE

GAS CHROMATOGRAPHY. By A. I. M. KEULEMANS. Edited by C. G. VERVER. Second Edition. Pp. xxii + 234. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1959. Price $7.50; 60s.

The new edition of this outstanding volume on gas chromatography is a little disappointing in that, although most of the new developments in the technique are now included, their treatment is not as exhaustive as might have been expected from the high standard of the original work. The description of capillary columns, although an excellent summary of their important features, gives little impression of the considerable effort being put into their development. Similarly, the new section in Chapter 3 on ionisation detectors does not mention the more refined micro-argon detector or the single-jet flame detector.

In spite of these minor criticisms, the book well maintains its authoritative position in the field and is essential to those making a detailed study of the technique. The presentation generally is clear and concise, and the author's considerable experimental experience makes the text extremely interesting and stimulating. The new introduction to Appendix 1 gives a timely warning against the indiscriminate multiplication of stationary phases and should encourage the standardisation of liquids and methods of presenting retention-volume data. The addition of a subject index is very welcome, and the editor is to be congratulated on the absence of errors.

D. H. DESTY

CHEMICAL ANALYSIS OF RESIN-BASED COATING MATERIALS. Edited by C. P. A. KAPPELMEIER. Pp. xxviii + 630. New York and London: Interscience Publishers Inc. 1959. Price $19.50; 147s.

This book, edited by Dr. Kappelmeier, in his lifetime one of the world's recognised expert on this type of analytical work, is obviously intended to be a working laboratory reference book and as such admirably fills the bill. Although most of the book was written by a team of experts from America, Holland, Canada, Switzerland, Germany and England, the guiding hand of Dr. Kappelmeier can be clearly seen. The twenty-five contributors are all internationally known experts in their own fields and have produced between them a manual of practical methods of such value that no laboratory engaged in this type of work can afford to be without it.

The book begins with a detailed description of contents and proceeds in twenty-two chapters to cover most of the analytical aspects of oil-based coating materials, latex paints and lacquers. The specialised topics, with the notable exception of epoxy resin-based materials, appear to have been well covered in lucid detail, and methods for the analysis of these materials are described in a clear and concise form. Such of these methods as have been tried by the reviewer have proved to be adequate, clearly explained and easy enough to be carried out by personnel having only moderate training. Although the analysis of dried films of resin-based surface-coating materials has not been specifically dealt with in the text, many of the procedures described could be used for or adapted to such analyses.

The general treatment of the subject has been such that the book provides a summary of the work of numerous workers in this field of analysis; this has resulted in the production of a book based on sound theoretical knowledge supported by the results of practical experimentation and coupled with that practical basis upon which the success of all chemical analyses depends. If it is true that chemical analysis is one of the eyes through which research sees its way forward, then this book is the eye through which can be seen the solution to many of the problems of the surface-coating industry. Obviously no book can cover methods of analysis capable of solving all the problems, but this book should act as a pointer and a spur to workers, enabling them to approach their problems armed with the best practical knowledge.

The book is well written in good English, well produced on good paper and adequately illustrated and referenced. It should be well received in the industries to which it is directed and should be regarded as a notable contribution to the published knowledge on this subject, particularly as between its covers will be found this up-to-date collection of methods derived from such expert sources. At the price of 147s. it is value indeed. S. F. CHANCELLOR

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This translation will appear in monthly parts corresponding to those of the Russian original. The publication is supported by the Department of Scientific and Industrial Research, and the translations are supplied by Infosearch Ltd., London.

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REPRINTS FROM *THE ANALYST*

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